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Elemental Analyses of Lunar Samples by
14 MeV and Thermal Neutron Activation

Final Report for Period Ending
January 31, 1971
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- ✓VII. Publication - Instrumental Activation Techniques for the Analysis of Meteorites and Lunar Materials, American Laboratory September, 19-31 (1970).
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SECTION I

Elemental Analyses of Lunar Samples by 14 MeV and Thermal Neutron Activation

ABSTRACT

Instrumental 14 MeV neutron activation analysis was used to determine the abundance of major elements in 28 samples collected by the Apollo 11 Mission and 19 samples derived from material collected by the Apollo 12 Mission. The elements determined include O, Si, Al, Mg, and Fe.

Abundances of other minor and trace elements have also been determined by use of thermal neutron irradiations and gamma-gamma coincidence spectrometry. Implications of the data to the understanding of the geochemistry of the moon are discussed in various publications of this group included with this report.

INTRODUCTION

This report constitutes the final report on Contract NAS 9-8017 for the period ending January 31, 1971. It consists largely of a collection of reprints and manuscripts generated by the group during 1970 and 1971, to date. A majority of the previously unpublished material is included in Section II which is a manuscript of the paper presented by Dr. W. D. Ehmann at the Apollo 12 Lunar Science Conference in Houston, Texas, on January 11, 1971. This manuscript is being expanded to include additional data and discussion. It will be submitted in its longer form for publication in Supplement II of Geochimica et Cosmochimica Acta to be published by M.I.T. Press. Other unpublished data on various minor and trace elements are still being processed and will be published later.

We wish to point out that the O abundances reported in our papers are the only direct determinations of O reported on lunar samples that have not been exposed to the atmosphere. The only other group reporting direct O determinations did not process their samples in an inert atmosphere and their abundances may reflect atmospheric contamination (Wanke, 1971 - Private communication). We also note with some pride that a recent compilation of data on the lunar rocks (Mason, 1970 - The Lunar Rocks) in listing prime abundance data has selected our reported data for the elements O, Si, and Al.

The Contract personnel for the period of this report were: Principal Investigator - Dr. William D. Ehmann, Professor of Chemistry; Co-Investigator - Dr. John W. Morgan, Research Associate; and Mr. David E. Gillum, Research Associate (filling this position for the period September 1970 through January 1971 after the departure of Dr. Morgan). Mr. Stephan Cox assisted with the computer work on a part-time basis.

Financial records for the contract have been kept by the University of Kentucky Research Foundation and may be obtained by contacting:

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Major Element Abundances in Apollo 12 Rocks
and Fines by 14 MeV Neutron Activation

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Abstract. Abundances of O, Si, Al, Mg, and Fe in seven rocks and four samples of fines collected by the Apollo 12 mission have been determined by instrumental 14 MeV neutron activation. These five elements constitute approximately 90% of the mass of these materials. The abundances for Type A, Type AB, Type B, and Type D, respectively, are: O-39.3, 39.4, 40.4, 42.0%; Si-20.7, 21.2, 21.4, 23.0%; Al-4.3, 5.1, 4.8, 6.7%; Mg-6.9, 4.5, 4.5 to 10.1, 6.6%; Fe-15.5, 14.7, 15.1, 12.6%. These results and separately published results [Morgan and Ehmann, 1970b] on five chips derived from rock 12013 are discussed and compared to the results obtained on the Apollo 11 materials.

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(Paper to be presented at the Second Lunar Science Conference, Houston, Texas, January 11, 1971. This work has been supported by N.A.S.A. Contract NAS 9-8017).

INTRODUCTION

Activation analysis employing 14 MeV neutrons has been used to determine the abundances of O, Si, Al, Mg, and Fe in rocks and fines collected during the Apollo 12 mission. This method of analysis has been shown to yield accurate and precise abundance data while retaining the advantage of speed. The method is essentially non-destructive, except for very minor levels of radioactivity induced in the samples and radiation damage. We regard this as the most reliable method available for the direct determination of O in bulk samples.

Analyses of Apollo 11 lunar rocks and fines using these techniques have been reported by Ehmann and Morgan [1970]. The more important observations based on our analyses of the Apollo 11 materials are:

- (1) The crystalline rocks fall into two distinct chemical groups based on their Al abundances. These chemical groups are independent of crystal texture.

- (2) The breccias and fines are enriched in O, Si, and Al, as compared to the crystalline rocks and must contain components distinct in their composition from the crystalline rocks.

- (3) The breccias and fines exhibit an apparent O deficiency of approximately 1.6% O, as compared to the calculated O abundance required for simple stoichiometry based on total silicate analyses. This may be due to reduction and subsequent O depletion of the fines and breccias due to the action of solar wind hydrogen. The crystalline rocks exhibit little or no O depletion based on stoichiometry.

(4) Si and O are strongly correlated in the Apollo 11 rocks following the regression line represented by the equation: $O\% = 1.15 Si\% + 18.2$. This regression line has a slope significantly different than that reported by Eugster [1969] for terrestrial igneous rocks. The low O/Si ratio in the lunar rocks is in part due to the presence of ilmenite (31.6% O) and reduced species such as Ti(III), but the difference in the slopes of the terrestrial and lunar regression lines is not simply explained.

In this paper the results of the analyses on Apollo 12 rocks and fines are examined in light of these observations on Apollo 11 materials.

ANALYTICAL METHOD

Apparatus. 14 MeV neutrons were produced by a Kaman Nuclear model A-1250 Cockcroft-Walton generator, and the neutron yield monitored by a low geometry enriched BF_3 detector. The pneumatic single sample transfer system, using dry N_2 as propellant gas, and the sequential programming circuit are essentially those described by Vogt et al. [1965]. Minor modifications were made to interface with a data acquisition system based on a Nuclear Data ND 2201 4096 channel analyzer. Gamma-ray activity measurements were made using a 10 cm x 10 cm well type NaI(Tl) detector.

Preparation of samples. Samples of lunar rocks were received under a double dry nitrogen seal as irregular-shaped chips, ranging in weight between 0.48 and 2.1g. The design of our usual polyethylene rabbits [Ehmann and McKown, 1968] was modified to take 3/8 in.i.d. capsules. Before use, all polyethylene parts for the

rabbit assembly were immersed in absolute ethanol and agitated ultrasonically for 20 minutes. They were dried in a jet of high purity dry N_2 , transferred to a vacuum desiccator, and dried under vacuum. Samples were transferred to inner capsules in a glove box under dry N_2 . After sealing, the capsule was positioned in the outer container with polyethylene spacers, so that the apparent center-of-mass was centered in the neutron beam position. The outer container was flushed with dry N_2 before it, too, was sealed.

Preparation of standards. The encapsulation of the standards was identical to that described for the samples. Fused optical quartz L-1 (pieces of a broken quartz lens donated by Dr. W. Blackburn of the University of Kentucky) was used as a standard for Si and O. Potassium dichromate NBS#136b was used, as received, for an additional standard for the O determinations. In addition to powdered standards, chunks of L-1 quartz, similar in shape to the rock chips, were prepared. Initially, these were used together with powdered standards for Si and O analyses, until it was established that geometry effects introduced no detectable systematic bias. For O, a two way comparison was possible, with powdered quartz and NBS#136b $K_2Cr_2O_7$. The quartz chunks agreed with both of these to an accuracy of about 0.4 relative per cent.

Opal glass (NBS#91) and potassium feldspar (NBS#70a) were dried at $110^\circ C$ and used for Al standards. The abundances of this element in these materials bracket those reported in the lunar samples. In addition, these standard materials contain Si as a major constituent and this element produces a primary interference in the Al determination. A correction for this interference was made specifi-

cally for each analysis using the measured Si content of the appropriate samples. The apparent Al abundance of the standards was also adjusted accordingly. Any residual error in the estimation of this correction will be largely self cancelling for samples and standards possessing similar Al/Si ratios.

Standards for Mg and Fe were NBS#88a dolomitic limestone (dried at 110°C for two hours) and reagent grade ferrous ammonium sulfate, respectively.

Procedures. Detailed procedures for the determination of Si and O have previously been given by Morgan and Ehmann [1970a]. Procedures for Al, Mg, and Fe have been outlined in Morgan and Ehmann [1971], along with a detailed discussion of the analytical principles and potential interferences. These procedures have been shown to yield precise and accurate data for these elements, based on analyses of selected U.S.G.S. standard rocks.

Special care was taken to handle all lunar rocks and fines under a high purity dry N₂ atmosphere. Therefore, it is felt the O data presented here closely reflect the true abundance of O under lunar conditions.

Results. The results of the analyses of seven Apollo 12 crystalline rocks and four samples of fines are presented in Table 1. The error limits for the individual rocks are standard deviations of the means based typically on eight replicate analyses for O, seven replicate analyses for Si, and three replicate analyses for Al, Mg, and Fe. The error limits for the group means are standard deviations of the mean, based on the distribution of

the individual values within each group. Previously published results [Morgan and Ehmann, 1970b] on five chips of Apollo 12 rock 12013 are summarized in Table 2. All abundances are given in units of weight per cent.

Table 3 compares the Apollo 11 and the Apollo 12 data, as obtained in our laboratory. Analyses for Mg and Fe were not done on rock 12013 due to the small size of the chips and the very limited time available to us to complete the analyses of the chips and pass them to other investigators for further analyses. The time factor also prevented determination of these two elements in the Apollo 11 rocks which were part of a cooperative analysis scheme [Goles et al., 1970].

DISCUSSION

Chemical groupings in Apollo 12 rocks. The Apollo 11 crystalline rocks were found to fall into two distinct groups based on their Al abundances [Ehmann and Morgan, 1970]. As can be seen from Table 1, the situation is not as clear for the Apollo 12 rocks. However, a similar chemical grouping is suggested with rocks 04, 63, 22, and 35 exhibiting Al abundances similar to the low Al group from Apollo 11 and rocks 21, 64, and 51 exhibiting Al abundances similar to the high Al group. Additional Al determinations on other Apollo 12 rocks would be useful, however, in confirming the existence of distinct groups.

The Apollo 12 crystalline rocks and fines exhibit a significant (99% confidence level) positive correlation for Al and Si. This may be interpreted as an increase in feldspar with differentiation and a further enrichment in the fines due to the addition

of anorthosite. The Al-Si regression line for the Apollo 12 rocks and fines connects directly with the Al-Si regression line for rock 12013, but Al becomes negatively correlated with Si in the 12013 chips [Morgan and Ehmann, 1970b]. This negative correlation could be explained by intrusion of a compacted soil by a liquid rich in Si (plus some potassium feldspar).

The unusual mineralogy of the troctolite (rock 12035,04) is reflected in the high abundances of Mg and Fe found. The Lunar Sample Preliminary Examination Team [1970] reports a composition consisting of 15% pyroxene, 40% olivine, and 45% plagioclase for this rock.

Fines. The Apollo 12 data presented here suggest that the fines are not derived exclusively from the crystalline rocks sampled, but represent rather complex mixtures. Material of anorthositic composition would be required in the fines to account for the higher Al abundance in the fines (6.7% Al), as compared to a simple 50-50% mixture of Type A and B crystalline rocks (4.6% Al). Using the data presented here an approximately 17% admixture of average anorthositic material (16.2% Al) similar to that reported by Wood et al. [1970] would be required to account for the Al abundance in the fines. Ganapathy et al. [1970] have estimated a 1.7% admixture of meteoritic matter in the Apollo 12 fines and have noted that an additional admixture of 10% of material similar to rock 12013 would account for the high Rb, Cs, and U abundances in the fines. The calculation of the anorthositic contribution as made above based on Al is rather insensitive to the amount of 12013 material present (6.5% Al) and the small

amount of meteoritic matter. However, a mixture of 2% meteoritic matter, 71% average A and B rock, 17% anorthositic material, and 10% rock 12013 material does yield a composition for the fines almost identical to that found experimentally for the elements Al and Fe. Abundances of Mg and Si calculated in the same manner are about 1% lower than found experimentally, suggesting the requirement of still another component. Additional speculations concerning the composition of the fines is not warranted pending detailed mineralogical studies.

Oxygen in the moon and the earth. O and Si are found to exhibit a significant (99% confidence level) positive correlation (Fig. 1) in the Apollo 12 crystalline rocks according to the equation:

$$O\% = 0.96 Si\% + 19.6.$$

This regression line is nearly identical to that given by Ehmann and Morgan [1970] for the Apollo 11 rocks:

$$O\% = 1.15 Si\% + 18.2.$$

In both cases the slope of the regression line is significantly different than that given by Eugster [1969] for terrestrial igneous rocks:

$$O\% = 0.415 Si\% + 35.0.$$

The Apollo 12 rocks are generally higher in both O and Si, than the corresponding Apollo 11 rocks. This is probably a reflection of the generally lower ilmenite content of the Apollo 12 samples. The presence of ilmenite in the lunar samples results in a displacement of the O-Si regression line to the O deficient side of the line for the terrestrial rocks (ilmenite contains only 31.6% O),

but does not in itself explain the significant difference in the slopes of the lunar and terrestrial regression lines.

In contrast, Morgan and Ehmann [1970b] have shown that analyses of five chips of rock 12013 result in a O-Si regression line that closely parallels the terrestrial line:

$$\text{O}\% = 0.43 \text{ Si}\% + 33.0,$$

but represents rocks poorer by some 2% O. The differences exhibited among these several regressions must in part be related to the amount of O available during the course of the crystallization of the rocks.

An apparent O deficiency of approximately 1.6% O was noted in the Apollo 11 fines and breccias, as compared to the amount of O required for simple stoichiometry, based on total silicate analyses. At this writing the only complete analyses of the ^{Apollo 12} fines available is that reported by the Lunar Sample Preliminary Examination Team [1970]. Using their data for the elements not determined in this work, a calculated O abundance of 44.6% is obtained for the Apollo 12 fines, based on simple stoichiometry. The oxygen abundance determined experimentally in this work is only 42.0% O, suggesting an O depletion in the fines of some 2.6% O. A similar calculation for the Apollo 12 crystalline rocks yields a depletion of only 0.7% O. These calculations must be repeated when additional total silicate analyses become available, but our observation of an O depletion in the lunar fines based on the Apollo 11 data [Ehmann and Morgan, 1970] appears to be confirmed by the Apollo 12 data reported here.

Additional discussions of the data presented here in the light of information presented at the Second Apollo 12 Lunar

Science Conference will be published elsewhere [Ehmann and Morgan, 1971].

Acknowledgements. This work has been supported by N.A.S.A. Contract NAS 9-8017 and the University of Kentucky Research Foundation. The authors wish to express their thanks to Mr. D. E. Gillum and Mrs. Susan Smith for their assistance in data processing and the preparation of this manuscript.

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Caption for Fig. 1. Relation of Si and O¹ in lunar materials.
The line for terrestrial igneous rocks is based on Eugster [1969].

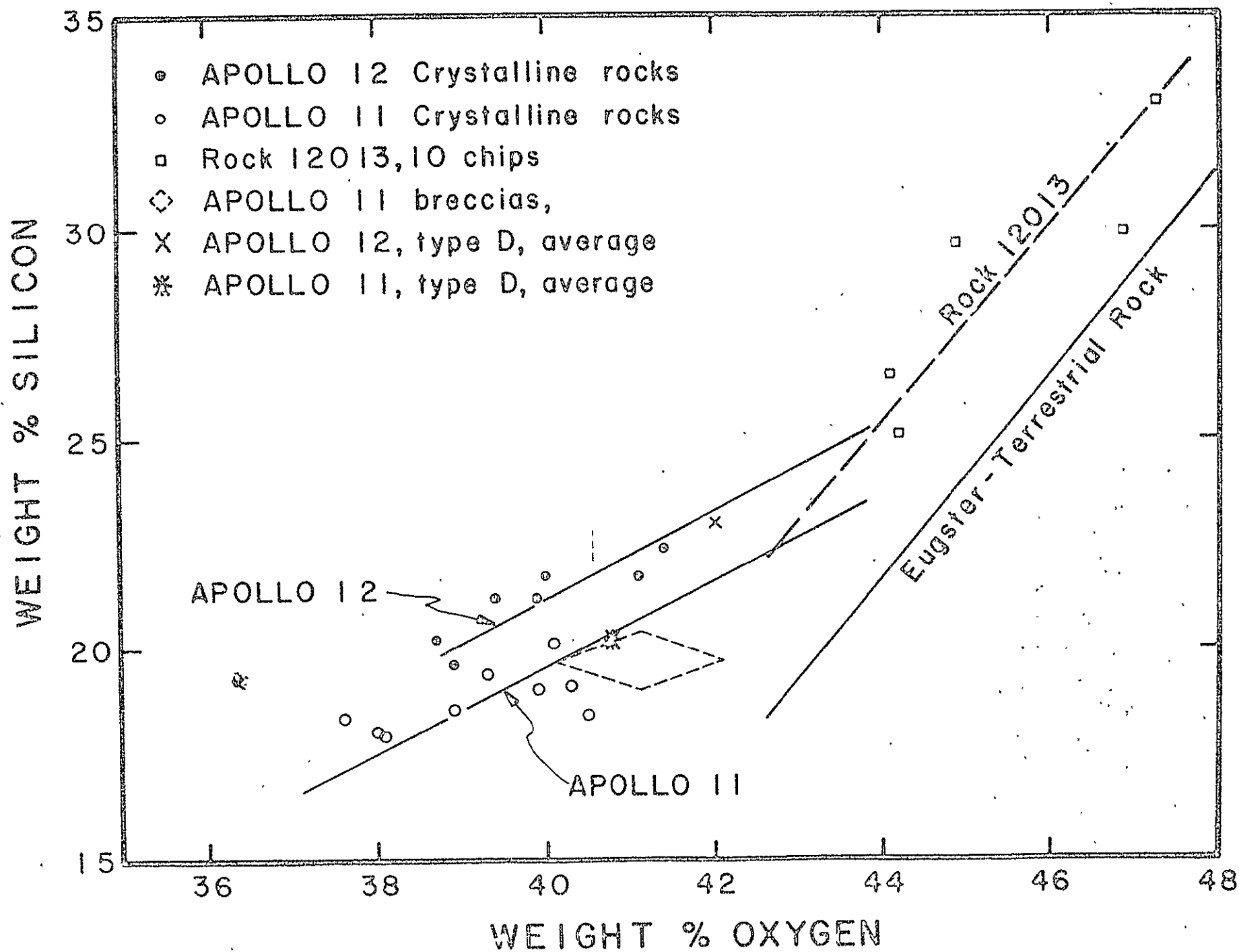


TABLE 1. Major Elements in Apollo 12 Rocks and Fines.

Rock	Type	%O	%Si	%Al	%Mg	%Fe	Total
04,32	A	39.9 \pm 0.2	21.2 \pm 0.2	4.38 \pm 0.03	7.3 \pm 0.4	15.1 \pm 0.1	87.9
63,60	A	38.7 \pm 0.4	20.2 \pm 0.2	4.23 \pm 0.06	6.5 \pm 0.2	15.9 \pm 0.2	85.5
<u>MEAN</u>	A	39.3 \pm 0.6	20.7 \pm 0.5	4.31 \pm 0.08	6.9 \pm 0.4	15.5 \pm 0.4	86.7
51,46	AB	39.4 \pm 0.2	21.2 \pm 0.2	5.11 \pm 0.09	4.5 \pm 0.1	14.7 \pm 0.2	84.9
21,81	B	40.0 \pm 0.1	21.7 \pm 0.1	5.54 \pm 0.05	4.6 \pm 0.1	14.2 \pm 0.7	86.0
22,53	B	38.9 \pm 0.1	19.6 \pm 0.1	4.04 \pm 0.01	6.1 \pm 0.4	15.1 \pm 0.4	83.7
35,04	B	41.1 \pm 0.2	21.7 \pm 0.1	4.35 \pm 0.01	10.1 \pm 0.3	16.0 \pm 0.6	93.3
64,34	B	41.4 \pm 0.2	22.4 \pm 0.2	5.46 \pm 0.05	4.5 \pm 0.4	15.1 \pm 0.4	88.9
<u>MEAN</u>	AB&B	40.2 \pm 0.5	21.3 \pm 0.5	4.90 \pm 0.30	6.0 \pm 1.1	15.0 \pm 0.3	87.4
32,34	D	41.9 \pm 0.3	23.9 \pm 0.2	7.29 \pm 0.09	6.5 \pm 0.6	12.4 \pm 0.8	92.0
44,18	D	42.0 \pm 0.2	23.2 \pm 0.2	6.51 \pm 0.06	7.3 \pm 0.7	14.2 \pm 0.3	93.0
57,79	D	42.8 \pm 0.3	23.0 \pm 0.1	6.58 \pm 0.18	6.4 \pm 0.5	12.3 \pm 1.1	91.1
70,70	D	41.4 \pm 0.2	22.0 \pm 0.2	6.59 \pm 0.03	6.3 \pm 0.1	11.5 \pm 0.3	87.8
<u>MEAN</u>	D	42.0 \pm 0.3	23.0 \pm 0.4	6.74 \pm 0.18	6.6 \pm 0.2	12.6 \pm 0.6	91.0

Error limits for individual rocks are the standard deviations of the means for replicate analyses. Error limits for the group means are standard deviations of the means, based on the distribution of values for the individual rocks within each group. See text for details.

TABLE 2. O, Si and Al in Apollo 12 Rock 12013
[Morgan and Ehmann, 1970b]

Chip Number	Sample Weight (mg)	%O	%Si	%Al
10,06	88	44.2 [±] 0.3	25.1 [±] 0.1	7.1 [±] 0.3
10,15	99	44.9 [±] 0.5	29.6 [±] 0.2	6.6 [±] 0.1
10,18	66	46.9 [±] 0.4	29.9 [±] 0.1	6.3 [±] 0.2
10,41	32	47.3 [±] 0.4	33.0 [±] 0.4	5.1 [±] 0.3
10,44	42	44.1 [±] 0.3	26.5 [±] 0.1	6.3 [±] 0.6
MEAN (MASS WEIGHTED)		45.2 [±] 0.6	28.4 [±] 1.3	6.5 [±] 0.3

Error limits are standard deviations of the means of 6-8 replicate analyses for O and Si and 3 replicate analyses for Al. The error limits for the means are standard deviations reflecting the dispersion of the individual chip abundances.

TABLE 3. Comparison of Apollo 11 and 12 Analyses*

Material	%O		%Si		%Al		%Mg	%Fe
	-11-	-12-	-11-	-12-	-11-	-12-	-12-	-12-
Type A	38.5	39.3	18.9	20.7	4.0	4.3	6.9	15.5
Type B	39.4	40.2	18.7	21.3	5.0	4.9	6.0	15.0
Type C	41.1	--	19.7	--	6.6	--	--	--
Type D	40.8	42.0	20.2	23.0	7.2	6.7	6.6	12.6
Rock 12013		45.2		28.4		6.5	--	--

* Mg and Fe were not determined in the Apollo 11 materials, or rock 12013, due to time restrictions required by cooperative analysis schemes.

SECTION III

EARTH AND PLANETARY SCIENCE LETTERS 9 (1970) 164-168. NORTH-HOLLAND PUBLISHING COMPANY

LUNAR ROCK 12013; O, Si, Al and Fe ABUNDANCES

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The abundances of O, Si, Al, and Fe have been determined by 14 MeV neutron activation analysis in 5 chips and 3 powders derived from Apollo 12 lunar rock 12013. These four elements constitute approximately 90% of the mass of this rock. Mass weighted mean abundances in weight per cent for the five chips where contamination problems are expected to be minimal are:

O: 45.2%, Si: 28.4%, Al: 6.5%, and Fe: 10%.

A significant positive correlation was observed for Si and O abundances in the chips and a linear regression line drawn through these data passes close to the mean for the Apollo 11 breccias. A significant negative correlation was observed for Al with Si in the chips.

1. Introduction

Apollo 12 lunar rock 12013 has a composition that clearly distinguishes it from all other rocks returned by the Apollo 11 and 12 missions. It is described as being similar to a late-stage basaltic differentiate, which does not resemble terrestrial diorites, dacites, anorthosites, or tektites in most elemental abundances [1]. O'Keefe [2], however, has pointed out that the major element composition of the glassy portion of rock 12013 is more like some tektites from Java than like any terrestrial igneous rock.

Rock 12013 is extremely heterogeneous and bears some similarity to a volcanic tuff or breccia [3]. Due to the modest weight of this rock (82 g) and its heterogeneity special care was taken to obtain the maximum amount of data on small samples selected to be representative of the various compositional regions within the rock.

A group of five chips and two powders derived from slice 10 of rock 12013 (see plate 1). These samples along with a small sample of "sawdust" derived from the original cutting of rock 12013 were allocated to a cooperative analysis scheme involving

groups at the University of Kentucky, Oregon State University, and the University of Chicago. The samples were first received by the writers and subjected to 14 MeV neutron irradiation for the non-destructive determination of the major rock-forming elements O, Si, Al and Fe. The samples were then transferred to R.A.Schmitt at Oregon State University for non-destructive thermal neutron activation analysis, and finally to E.Anders at the University of Chicago for additional trace element determinations via thermal neutron activation analysis and radiochemical separation.

The extensive sequential analytical procedures followed on the same rock samples should provide coherent data which would have been difficult to obtain in any other way. This paper presents only the data obtained by the 14 MeV neutron activation portion of this cooperative scheme of analysis. The thermal neutron activation data of the groups at Oregon State University and the University of Chicago on the same samples are presented in separate papers in this issue.

More detailed descriptions of the samples may also be found elsewhere in this issue.

2. Experimental

Details of the experimental procedures used for the determination of O, Si, Al, and Fe by 14 MeV neutron activation may be found in previous publications of this group [4, 5]. The five chip samples were received under a dry nitrogen atmosphere and were sealed in polyethylene irradiation vials in an atmosphere of dry nitrogen. Powders 10, (37 + 24) and 10, 35 were exposed to the atmosphere briefly during packaging, but the vials were flushed with dry nitrogen prior to and after filling.

The powder samples were prepared from interior samples which had been cleaned with acetone and powdered in a stainless steel mortar prior to their receipt in our laboratories. Since alteration of the abundances of O and Fe might be expected in these powder samples, the data on the powders are not included in the mean abundances computed. Powder 12013, 17 is sawdust derived from wire sawing of the rock. This sample is expected to be highly contaminated with residue from the Cu-Fe-diamond saw wire.

3. Results and discussion

The abundances of O, Si, Al and Fe in samples of rock 12013 are given in table 1. The data for O and Si are based on 7 to 9 replicate analyses and the data for Al and Fe are based on 3 replicate analyses. The error limits stated are the standard deviations of the mean of the replicate analyses. The mean abundances in the five chips have also been computed by mass-weighting the individual chip data, as an approximation to the whole rock abundances.

Data for U.S.G.S. standard rock BCR-1 are included to provide an index of the accuracy of the method. The BCR-1 data for Al and Fe were obtained simultaneously with the rock 12013 data presented here. The Si and O data were obtained previously on the same samples using the same standards [4]. The agreement with compilation values of Flanagan [6] is quite satisfactory.

Due to the very small sample sizes used in this study the Fe determinations reported here should be treated with reservations in spite of the excellent agreement

Table 1
Elemental abundances in Lunar Rock 12013.

Sample designation	Sample weight (mg)	O	Abundance-wt.% *		Fe
			Si	Al	
<i>Chips</i>					
10, 06	88	44.2 ± 0.3	25.1 ± 0.1	7.1 ± 0.3	11 ± 1
10, 15	99	44.9 ± 0.5	29.6 ± 0.2	6.6 ± 0.1	9 ± 1
10, 18	66	46.9 ± 0.4	29.9 ± 0.1	6.3 ± 0.2	10 ± 1
10, 41	32	47.3 ± 0.4	33.0 ± 0.4	5.1 ± 0.3	11 ± 1
10, 44	42	44.1 ± 0.3	26.5 ± 0.1	6.3 ± 0.6	9 ± 1
<i>Mean (weighted by mass — chips only)</i>		45.2 ± 0.6	28.4 ± 1.3	6.5 ± 0.3	10 ± 0.4
<i>Powders</i>					
10, (37 + 24)	17	44.0 ± 0.8	28.4 ± 0.2	6.9 ± 0.1	13 ± 1
10, 35	20	40.4 ± 0.9	24.9 ± 0.4	6.5 ± 1.1	16 ± 4
17 (sawdust)	37	33.7 ± 0.5	18.2 ± 0.1	4.9 ± 0.3	8 ± 1
<i>Standard Rock BCR-1</i>					
This work **		45.8 ± 0.2	25.7 ± 0.3	7.0 ± 0.1	9.6 ± 0.2
Compilation of Flanagan [6]		45.5	25.5	7.2	9.5

* Error limits given are standard deviations of the mean of 6 to 8 replicate analyses for O and Si and 3 replicate analyses for Al and Fe.

** Data for Al and Fe obtained during this series of analyses. Data for Si and O obtained previously [4] using the same samples and standards.

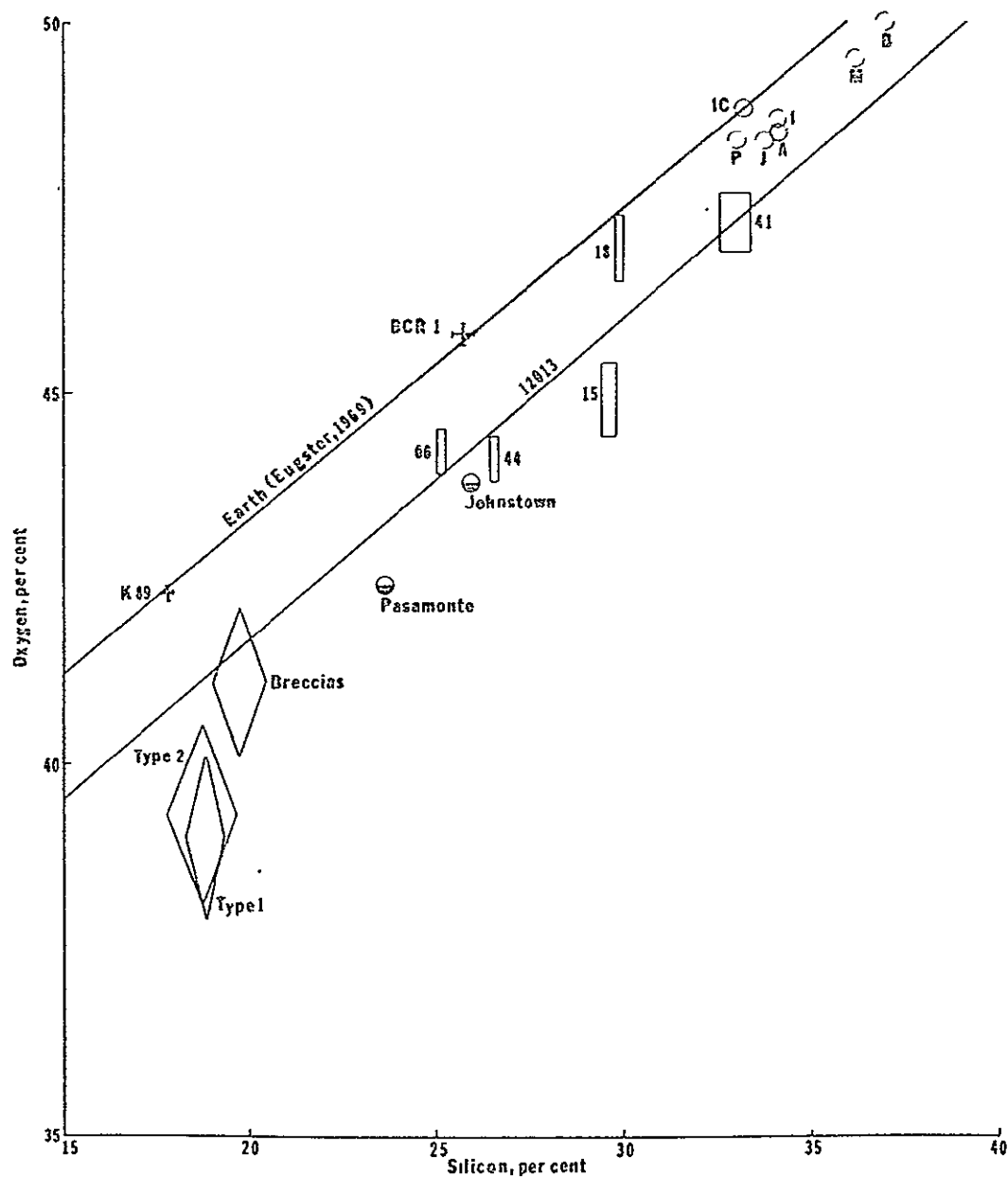


Fig. 1. Variation diagram of O versus Si. The rectangles are experimental results for five chips from slice #10 of lunar rocks 12013, and are labelled with the appropriate sample number. The size of the rectangles represents the standard deviation of the mean calculated from replicate runs. The diamonds are Apollo 11 breccias and type 1 and type 2 crystalline rocks [5]. The size represents the standard deviation of the mean based on the results for each rock chip analyzed. The small crosses are terrestrial comparison samples and the size represents the standard deviation of the mean for replicate splits of these powders. Open circles are tektites and the letters indicate the group, A = Australites, P = Philippinites, I = Indochinites, J = Javanites, B = Bediasites and other North American tektites IC = Ivory Coast tektites and M = Moldavites. Half-filled circles are two achondrites. The size of the circles has no significance. The line marked Earth (Eugster, 1969) indicates the trend observed in terrestrial igneous rocks [7]. The line marked 12013 is an unweighted regression calculated with Si as the independent variable.

obtained on BCR-1. The activity levels for Fe were low with the error due to counting statistics alone equal to approximately ± 10 relative percent. Since calculation of the Fe abundance involves several correction factors, the accuracy of the Fe determinations in these small samples is probably no better than ± 15 relative percent. The errors due to counting statistics for O and Al are between 3 and 5 relative percent, and for Si between 0.5 and 2 relative percent.

A correlation between Si and O has been found in terrestrial rocks [7], in six individual splits of the Allende chondrite [4], and in 27 Apollo 11 rocks [5]. In the case of the five 12013 rock chips, the relation of Si to O has been found to yield a correlation coefficient (r) of 0.88. A simple unweighted regression, taking Si as the independent variable yields,

$$\text{O \%} = 0.43 \text{ Si \%} + 33.0,$$

and is shown in fig. 1. The slope of this line is significant at the 95% confidence level ($t = 3.3$).

This line is virtually parallel to the regression constructed by Eugster [7], for terrestrial igneous rocks;

$$\text{O \%} = 0.42 \text{ Si \%} + 35.0,$$

but represents rocks poorer by some 2% O.

It could be argued that there is a systematic error in our analytical method, however, our analyses for the U.S.G.S. standard basalt BCR-1 and the N.A.S.A. Knippa basalt K89 are also plotted in fig. 1 and fall very closely on to Eugster's terrestrial line.

An extrapolation of the rock 12013 Si-O regression passes through the field defined by the Apollo 11 breccias. Inclusion of these rocks in the regression change the slope insignificantly ($t = 1.16$). The crystalline Apollo 11 rocks do not lie close to the 12013 regression line.

It has been suggested [8] that the deviation on a Si-O plot of the Apollo 11 regression line from Eugster's terrestrial line is simply due to the presence of ilmenite, which is relatively oxygen poor. Accordingly, the Apollo 11 abundances were recalculated to an ilmenite free basis using Ti abundances for the same samples [9]. The recalculation was found to simply move the Apollo 11 rocks along lines parallel to the terrestrial and 12013 lines. Obviously, the mineralogy does not control the Si-O plot in any

simple way. The reverse is surely the case, that is, that the mineralogy is very much controlled by the amount of oxygen available during the course of crystallization.

There are very few data for Si and O in achondrites. Results for Pasamonte and Johnstown [10] are shown in fig. 1. These two points lie close to the 12013 regression, but are below it by about the same amount as the mean of the Apollo 11 breccias.

It has been suggested [2] that rock 12013 may bear some chemical resemblances to tektites. Average analyses for all tektite groups were taken from Schnetzler and Pinson [11] and the O contents calculated from the oxides. The resulting mean abundances are also plotted in fig. 1.

There is evidence that the Ivory Coast tektites are of terrestrial origin [12], and this is supported by this tektite group falling on Eugster's line. Unfortunately, the position of the other tektites is less satisfactory, as they lie between the terrestrial and the rock 12013 lines. The non-destructive analysis of a large number of unpowdered tektite chips for O and Si by 14 MeV neutron activation could lead to a more realistic comparison.

The Al abundances in the five 12013 chips are negatively correlated with Si ($r = -0.85$) and O ($r = -0.76$). Regression lines constructed with Al as the dependent variable have a significant slope in the case of Si ($t = 2.8$) but not for O ($t = 2.0$). Negative correlations with SiO_2 in tektites are well known [11]. The Al-Si negative correlations in tektites [11] and the 5 portions of 12013 (14 MeV neutron activation) are sufficiently similar to warrant a closer, comparative examination.

The powders of rock 12013 were not included in the preceding discussion because of possible contamination. The two sources of contamination most likely to interfere in this work are O and Fe. In the Si-O correlations these would tend to act in opposite directions. If the powders are plotted on an Si-O variation diagram they would lie on the O-poor side of the 12013 chips line, indicating that the Fe contamination may be the more serious. Although the Fe analyses reported here are near the limit of detection, they do indicate somewhat higher Fe abundances in the powders than in the rock chips.

The sawdust is known to be heavily contaminated, however, it is clear from the analyses that the major contaminant cannot be Fe. If the sawdust is a truly

representative sample of 12013 which has been heavily contaminated, our analyses indicate a contamination level of about 25 to 30% by weight.

Further implications of the variations of O, Al, Si and Fe in the portions of rock 12013 will be discussed in a future paper dealing with our completed analyses of other Apollo 12 rocks and fines.

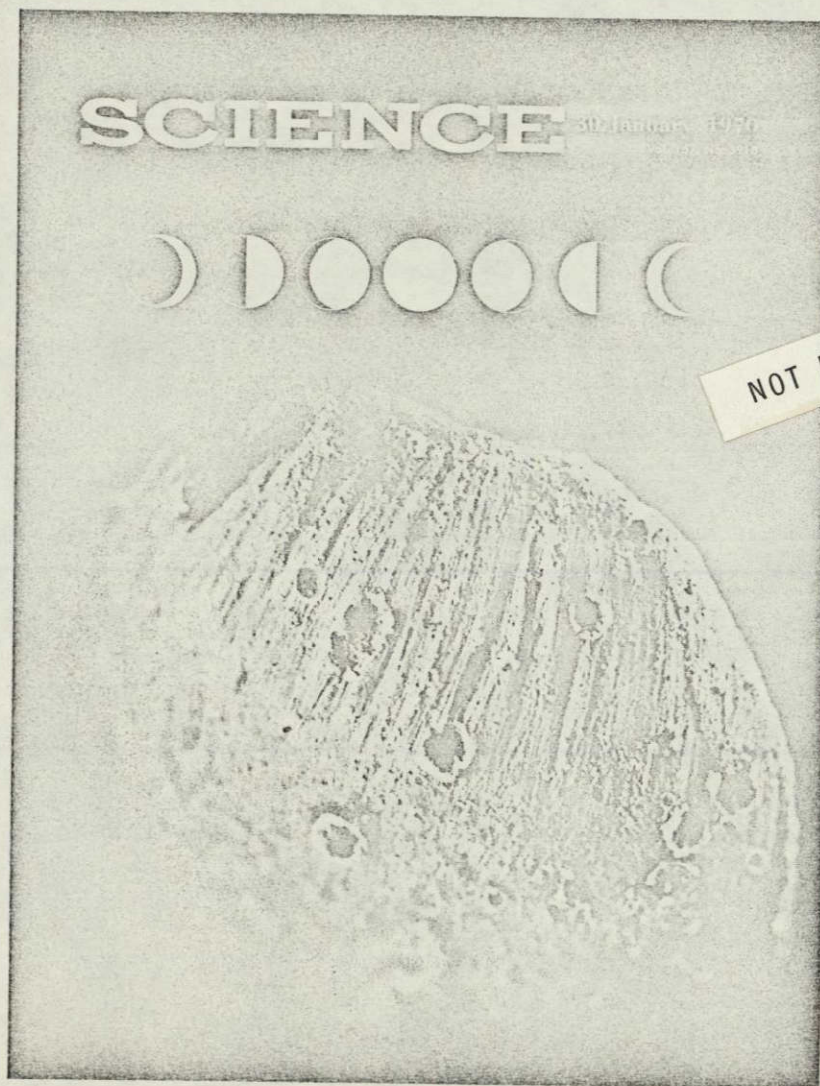
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Apollo 11 Lunar Science Conference



Oxygen, Silicon and Aluminum in Lunar Samples by 14 MeV Neutron Activation

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Oxygen, Silicon, and Aluminum in Lunar Samples by 14 MeV Neutron Activation

Abstract. *Abundances of oxygen, silicon, and aluminum in 27 lunar rocks and c aliquants of lunar soil have been determined by 14 MeV neutron activation. Mean abundances and standard deviations of individual abundances (in weight percent) within each type are: type A (2 rocks), 38.5 ± 1.2 oxygen, 18.9 ± 0.8 silicon, and 4.0 ± 0.4 aluminum; type B (7 rocks), 39.4 ± 1.0 oxygen, 18.7 ± 0.8 silicon, and 5.0 ± 0.6 aluminum; type C (18 rocks), 41.1 ± 1.0 oxygen, 19.7 ± 0.7 silicon, and 6.6 ± 0.5 aluminum; soil (3 aliquants), 40.8 ± 1.2 oxygen, 20.2 ± 0.2 silicon, and 7.2 ± 0.1 aluminum. Oxygen abundances are lower than those in most common terrestrial rocks and are comparable to those found in certain types of stony meteorites. From these results the lunar soil is most similar to the type C lunar rocks.*

The elements oxygen, silicon, and aluminum make up over 60 percent by weight of common terrestrial igneous rocks. The abundances of these major elements may be determined precisely and accurately by means of 14 MeV neutron-activation analysis. In addition, the technique is rapid and essentially nondestructive.

All lunar samples and comparator standards were packaged in heat-sealed polyethylene vials under a dry nitrogen atmosphere (1). Samples and standards were irradiated at fluxes of 10^8 to 10^9 neutrons $\text{cm}^{-2} \text{sec}^{-1}$ provided by a Kaman Nuclear A-1250 14 MeV neutron generator. A single sample transfer system employing nitrogen for the propellant gas was used (2). Samples and comparator standards were irradiated separately, and radioactivities were counted sequentially. Corrections for variations in the neutron flux were made by use of a BF_3 neutron monitor. Comparator standards for oxygen and silicon were powders and chunks derived from a piece of pure optical lens quartz. In-

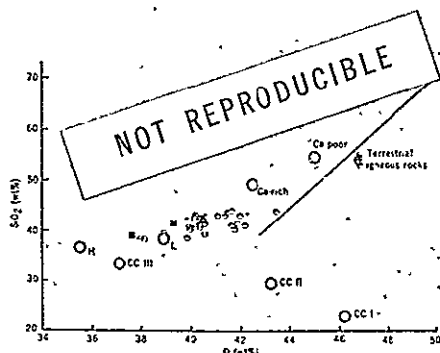
dependent standards of primary standard grade $\text{K}_2\text{Cr}_2\text{O}_7$ were also used for oxygen. Standards for aluminum were NBS 91 standard opal glass and NBS 70a standard feldspar. Samples of USGS standard rock BCR-1 and several basalts furnished by NASA were analyzed simultaneously with the lunar samples (3).

The nuclear reactions involved are: $^{28}\text{Si}(\text{n,p})^{28}\text{Al}$, $^{16}\text{O}(\text{n,p})^{16}\text{N}$, and $^{27}\text{Al}(\text{n,p})^{27}\text{Mg}$. Corrections for primary interference reactions and gamma-ray spectral interferences have been considered and applied where required. The most important corrections were applied in the determination of aluminum where the $^{30}\text{Si}(\text{n},\alpha)^{27}\text{Mg}$ reaction is a primary interference reaction and the $^{56}\text{Fe}(\text{n,p})^{56}\text{Mn}$ reaction provides a spectral interference. No corrections were applied for the primary interference reactions $^{31}\text{P}(\text{n},\alpha)^{28}\text{Al}$ in the determination of silicon and $^{19}\text{F}(\text{n},\alpha)^{16}\text{N}$ in the determination of oxygen. The target nuclides are likely to have relatively low abundances in lunar rocks based on preliminary analyses, but data presented

here may be adjusted later, if required, by noting that 0.1 percent fluorine is equivalent to 0.0415 percent oxygen and 1 percent P_2O_5 is equivalent to 0.21 percent silicon. The techniques used, which include a unique multiscale data-acquisition procedure for oxygen, have been reported (4). Application of these new techniques to analysis of the Pueblito de Allende chondrite (5) has shown that the standard deviations for six replicate analyses on a given aliquant ranged from ± 0.5 to ± 1.2 percent oxygen and from ± 0.11 to ± 0.24 percent silicon.

All calculations assume terrestrial isotopic abundances for these elements. The same 27 lunar rocks have been analyzed for numerous additional elements by others (6).

The most striking feature of these data (Table 1) is the depletion of oxygen in the lunar materials with respect to common terrestrial igneous rocks. Eugster (7) tabulated oxygen abundances in common terrestrial igneous rocks and noted that most analyses fell within the relatively narrow range of 40 to 50 weight percent oxygen. Only ultramafic igneous



rocks approach the mean oxygen abundances reported here. Eugster has found a good correlation for average compositions of common terrestrial igneous rocks as represented by the equation: $\%O = 0.194 \times \%SiO_2 + 35.0$ (equation 1). A least squares regression fitted to the pooled lunar rock data of this paper yields the equation: $\%O = 0.538 \times \%SiO_2 + 18.2$ (equation 2). A null hypothesis test of the significance of the slope yielded $t = 5.0$ (Student's t test), which is very significant at the 95 percent confidence level. The correlation coefficient for elemental silicon and oxygen is 0.71 (Fig. 1). The silicon and oxygen data, plotted in the manner of

Fig. 1. Relation of silicon as SiO_2 to oxygen in lunar rocks and soil. The line for terrestrial igneous rocks is taken from the tabulation of Eugster (7). Large circles represent mean abundances in various types of stony meteorites (11). Meteorite identification: CC I, II, and III are carbonaceous chondrites types I, II, and III, respectively; H represents high-iron ordinary chondrites and L represents low-iron ordinary chondrites. Ca-rich and Ca-poor refer to achondrites that are rich and poor in calcium, respectively. (■) type A rock; (○), type B rock; (○), type C rock; (■), soil; and the large circles represent meteorites.

Eugster, are shown in Fig. 1. Clearly, any line drawn through points representing the abundances in the three types of lunar rocks is distinct from the line based on terrestrial igneous rocks. A line based on equation 2 does pass close to the points defining the mean abundances in the CH- and CL-group ordinary chondrites.

The relative abundance of oxygen atoms to that of silicon atoms (atoms O/atoms Si) for the lunar rocks analyzed is 3.65 and for the lunar soil is 3.55. These values are similar to those found in the ordinary chondrites (CH = 3.9 and CL = 3.7) and to the value of 3.65 estimated for the earth as a whole (8). Gault *et al.* (9) had estimated this abundance ratio to be 3.1, based on remote analyses of the lunar surface. The corresponding value for the solar atmosphere is 29 (10).

In contrast to the situation for silicon and oxygen, both the absolute and atomic abundances of aluminum exhibit appreciable variation among rock types. The relative abundances of aluminum atoms to those of silicon atoms (atoms Al/atoms Si) are 0.22, 0.28, and 0.35 for types A, B, and C, respectively. This ratio for lunar soil is 0.36. Aluminum in lunar rocks is greatly enriched compared to the ordinary chondrites (atoms Al/atoms Si = 0.06), or any other chondrite group. On the basis of these data, the Apollo 11 lunar soil is most similar to type C lunar rocks. Rocks of types A and B would not appear to be the sole contributors to the formation of this lunar soil.

The precise silicon abundance data presented here should be of value in the computation of atomic abundances according to the accepted practice of reporting these relative to Si = 10^6 atoms. Abundances of iron may also be derived from our experimental data (3).

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Table 1. Oxygen, silicon, and aluminum abundances in lunar rocks by 14 Mev neutron activation. Error limits for individual samples are standard deviations of the means calculated generally on the basis of six replicate analyses for Si and O and two replicate analyses for Al. Error limits expressed for the type means are standard deviations based on values for the individual samples within the set.

Sample	Oxygen (%)	Silicon (%)	Aluminum (%)
Type A			
10022,32	39.3 \pm 0.4	19.4 \pm 0.1	4.2 \pm 0.1
10069,23	37.6 \pm 0.1	18.3 \pm 0.1	3.7 \pm 0.2
Mean	38.5 \pm 1.2	18.9 \pm 0.8	4.0 \pm 0.4
Type B			
10003,36	38.1 \pm 0.4	17.9 \pm 0.1	5.1 \pm 0.1
10024,20	38.9 \pm 0.1	18.5 \pm 0.1	4.1 \pm 0.2
10047,14	40.1 \pm 0.1	20.1 \pm 0.1	5.5 \pm 0.3
10050,29	40.5 \pm 0.5	18.4 \pm 0.1	5.3 \pm 0.2
10058,21	39.9 \pm 0.3	19.0 \pm 0.2	5.5 \pm 0.2
10062,28	38.0 \pm 0.2	18.0 \pm 0.2	5.3 \pm 0.1
10071,21	40.3 \pm 0.2	19.1 \pm 0.1	4.2 \pm 0.1
Mean	39.4 \pm 1.0	18.7 \pm 0.8	5.0 \pm 0.6
Type C			
10018,21	40.1 \pm 0.4	20.1 \pm 0.1	6.6 \pm 0.1
10019,11	39.9 \pm 0.2	18.9 \pm 0.1	6.5 \pm 0.2
10021,22	41.8 \pm 0.6	19.6 \pm 0.1	6.7 \pm 0.1
10048,32	39.8 \pm 0.2	18.1 \pm 0.1	6.1 \pm 0.1
10056,23	41.3 \pm 0.3	20.2 \pm 0.1	5.7 \pm 0.1
10059,30	40.0 \pm 0.1	19.1 \pm 0.1	6.4 \pm 0.1
10060,17	40.3 \pm 0.2	20.0 \pm 0.1	6.2 \pm 0.1
10061,32	41.7 \pm 0.2	18.9 \pm 0.1	6.7 \pm 0.1
10063,05	41.9 \pm 0.3	20.3 \pm 0.2	6.6 \pm 0.2
10064,10	40.5 \pm 0.4	19.4 \pm 0.1	5.9 \pm 0.1
10065,14	41.6 \pm 0.7	19.3 \pm 0.2	6.6 \pm 0.1
10066,05	41.0 \pm 0.2	20.2 \pm 0.1	6.9 \pm 0.1
10067,05	41.6 \pm 0.1	20.6 \pm 0.1	7.0 \pm 0.1
10068,20	40.3 \pm 0.3	19.3 \pm 0.1	6.3 \pm 0.2
10070,05	43.4 \pm 0.3	20.6 \pm 0.2	7.1 \pm 0.1
10074,05	42.1 \pm 0.5	19.3 \pm 0.1	7.0
10073,21	41.4 \pm 0.3	20.5 \pm 0.1	7.3 \pm 0.1
10075,06	40.4 \pm 0.2	19.8 \pm 0.3	7.4 \pm 0.1
Mean	41.1 \pm 1.0	19.7 \pm 0.7	6.6 \pm 0.5
Soil			
10084,50	42.2 \pm 0.5	20.4 \pm 0.1	7.2 \pm 0.2
10084,50	40.5 \pm 0.9	20.3 \pm 0.1	7.3 \pm 0.1
10084,50	39.8 \pm 0.5	20.0 \pm 0.2	7.1 \pm 0.1
Mean	40.8 \pm 1.2	20.2 \pm 0.2	7.2 \pm 0.1

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SECTION V

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Oxygen, silicon and aluminum in Apollo 11 rocks and fines by 14 MeV neutron activation

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Abstract—Fast neutron activation analysis of Apollo 11 lunar material yielded: Type A (2 rocks) 38.5% O, 18.9% Si, 4.0% Al; Type B (7 rocks) 39.4% O, 18.7% Si, 5.0% Al; Type C (18 rocks) 41.1% O, 19.7% Si, 6.6% Al; Type D (3 aliquants) 40.8% O, 20.2% Si, 7.2% Al and 12.4% Fe. The crystalline rocks (Types A and B) can be put into two distinct chemical groups on the basis of Al contents. The fines and breccias are significantly higher in O, Si, and Al than the crystalline rocks. An apparent deficiency in the fines of about 1% O may be due to reduction by solar wind H.

INTRODUCTION

THE 14 MeV neutron activation analyses for O, Si and Al reported here represent the first stage of a cooperative multielement activation analysis scheme for a large number of major, minor and trace elements (GOLES *et al.*, 1970). The 14 MeV neutron activation method is rapid, and, except for very minor residual radioactivity and radiation damage, is essentially non-destructive. It is probably the only reliable method available for the direct analysis of O in bulk samples, and indications of O depletion in the lunar surface (GAULT *et al.*, 1967), make such measurements of considerable importance. Both Si and Al are routinely reported in wet chemical whole rock analyses; however, there is general agreement (MASON, 1962) that the procedures, at least for Al, leave much to be desired. The rapidity of the activation method enabled the data collection portion of the analyses for these three elements to be carried out on 27 lunar rocks in a period of about three weeks, so that the samples could be transferred to the next laboratory with a minimum of delay.

ANALYTICAL METHOD

Apparatus

14 MeV neutrons were produced by a Kaman Nuclear model A-1250 Cockcroft-Walton generator, and the neutron yield monitored by a low geometry enriched BF_3 detector. The pneumatic single sample transfer system, using dry N_2 as propellant gas, and the sequential programming circuit are essentially those described by VOGT *et al.* (1965). Minor modifications were made to interface with a data acquisition system based on a Nuclear Data ND 2201 4096 channel analyzer. Gamma-ray activity measurements were made using a 10 cm \times 10 cm well type NaI (TI) detector.

Preparation of samples

Samples of 27 lunar rocks were received under a double dry nitrogen seal as irregular-shaped chips, ranging in weight between 0.45 and 2.4 g. The design of our usual polyethylene rabbits (EHMANN and MCKOWN 1968) was modified to take $\frac{3}{8}$ in. i.d. capsules. The lunar rocks fitted this larger capsule except for two (10048-32; 10061-32) which were sealed in polyethylene bags within the outer rabbit container. Before use, all polyethylene parts for the rabbit assembly were immersed in absolute ethanol and agitated ultrasonically for 20 minutes. They were dried in a jet of high purity dry N_2 , transferred to a vacuum desiccator, and dried under vacuum. Samples were transferred to

inner capsules in a glove box under dry N_2 . After sealing the capsule was positioned in the outer container with polyethylene spacers, so that the apparent center-of-mass was centered in the neutron beam position. The outer container was flushed with dry N_2 before it, too, was sealed.

One 5 g sample of lunar fines was received and three aliquants of about 1 g each were prepared under dry N_2 by quartering. Duplicate aliquants of BCR-1, Knippa basalt K89 and vesicular basalts VB-1 and VB-2 were also taken and made up in $\frac{3}{8}$ in. i.d. capsules so that the analytical conditions were closely comparable with those of the rocks.

Preparation of standards

The encapsulation of the standards was identical to that described for the samples. Fused optical quartz L-1 (pieces of a broken quartz lens donated by Dr. W. Blackburn of the University of Kentucky) was used as a standard for Si and O. Potassium dichromate NBS# 136b was used, as received, for an additional standard for the O determinations. In addition to powdered standards, chunks of L-1 quartz, similar in shape to the rock chips, were prepared. Initially, these were used together with powdered standards for Si and O analyses, until it was established that geometry effects introduced no detectable systematic bias. For O, a two way comparison was possible, with powdered quartz and NBS# 136b $K_2Cr_2O_7$. The quartz chunks agreed with both of these to an accuracy of about 0.4 relative per cent.

Opal glass (NBS# 91) and potassium feldspar (NBS# 70a) were dried at 110°C and used for Al standards. The abundances of this element in these materials just bracket those reported in the preliminary analyses of lunar samples (LSPET, 1969). In addition, these standard materials contain Si as a major constituent and this element produces a primary interference in the Al determination. A correction for this interference was made specifically for each analysis using the measured Si content of the appropriate samples. The apparent Al abundance of the standards was also adjusted accordingly. Any residual error in the estimation of this correction will be largely self cancelling for samples and standards possessing similar Al/Si ratios.

Procedure

Detailed procedures for the precise determination of Si and O are given by MORGAN and EHMANN (1970). The chemical composition of the Apollo 11 rocks and fines is such that interferences are insignificant for O and Si determinations. Slight changes were made to increase the speed of analysis. The dwell time used for multi-scaling in the O analyses was increased from 0.4 sec to 0.8 sec to reduce the number of channels used. In the Si determinations, counting time was shortened from 300 sec to 150 sec, after calculation showed that the precision would not be significantly affected.

Aluminum analyses were made using the 0.84 MeV gamma-ray of ^{27}Mg . Appropriate correction was made for the primary interference from the reaction $^{30}Si(n, \alpha)^{27}Mg$. Samples and standards were irradiated for 1 min, and, following a delay of 300 sec to allow decay of ^{28}Al , were counted for 300 sec. The significant interference from the 0.85 MeV gamma-ray of ^{56}Mn was empirically determined by recounting after a delay of about 100 min. In principle, Fe analyses can be based on the ^{56}Mn activity, but these were made only for the lunar fines, using the Knippa basalt K89 as a standard. Taking the Fe abundance of this rock as 9.4 per cent, the means of triplicate analyses on each of three aliquants of fines were 12.6 per cent, 12.3 per cent and 12.3 per cent. The mean of these values, $12.4 \pm 0.2\%$ Fe, is in good agreement with the results obtained by other workers.

Results

The results for O, Si and Al in 27 lunar rocks and 3 aliquants of fines are given in Table 1. The O results are the mean of from 5 to 12 replicate runs and for Si 5-8

Table 1. Oxygen, silicon and aluminum abundances in individual Apollo 11 lunar rocks and lunar fines by 14 MeV neutron activation

N.A.S.A. No	Oxygen (wt. %)*	Silicon (wt. %)*	Aluminum (wt. %)*
<i>Type A</i>			
10022-32	39.3 ± 0.4	19.4 ± 0.1	4.2 ± 0.1
10069-23	37.6 ± 0.1	18.3 ± 0.1	3.7 ± 0.2
Mean	38.5 ± 1.2	18.9 ± 0.8	4.0 ± 0.4
<i>Type B</i>			
10003-36	38.1 ± 0.4	17.9 ± 0.1	5.1 ± 0.1
10024-20	38.9 ± 0.1	18.5 ± 0.1	4.1 ± 0.2
10047-14	40.1 ± 0.1	20.1 ± 0.1	5.5 ± 0.3
10050-29	40.5 ± 0.5	18.4 ± 0.1	5.3 ± 0.2
10058-21	39.9 ± 0.3	19.0 ± 0.2	5.5 ± 0.2
10062-28	38.0 ± 0.2	18.0 ± 0.2	5.3 ± 0.1
10071-21	40.3 ± 0.2	19.1 ± 0.1	4.2 ± 0.1
Mean	39.4 ± 1.0	18.7 ± 0.8	5.0 ± 0.6
<i>Type C</i>			
10018-21	40.1 ± 0.4	20.1 ± 0.1	6.6 ± 0.1
10019-11	39.9 ± 0.2	18.9 ± 0.1	6.5 ± 0.2
10021-22	41.8 ± 0.6	19.6 ± 0.1	6.7 ± 0.1
10048-32	39.8 ± 0.2	18.1 ± 0.1	6.1 ± 0.1
10056-23	41.3 ± 0.3	20.2 ± 0.1	5.7 ± 0.1
10059-30	40.0 ± 0.1	19.1 ± 0.1	6.4 ± 0.1
10060-17	40.3 ± 0.2	20.0 ± 0.1	6.2 ± 0.1
10061-32	41.7 ± 0.2	18.9 ± 0.1	6.7 ± 0.1
10063-05	41.9 ± 0.3	20.3 ± 0.2	6.6 ± 0.2
10064-10	40.5 ± 0.4	19.4 ± 0.1	5.9 ± 0.1
10065-14	41.6 ± 0.7	19.3 ± 0.2	6.6 ± 0.1
10066-05	41.0 ± 0.2	20.2 ± 0.1	6.9 ± 0.1
10067-05	41.6 ± 0.1	20.6 ± 0.1	7.0 ± 0.1
10068-20	40.3 ± 0.3	19.3 ± 0.1	6.3 ± 0.2
10070-05	43.4 ± 0.3	20.6 ± 0.2	7.1 ± 0.1
10073-21	41.4 ± 0.3	20.5 ± 0.1	7.3 ± 0.1
10074-05	42.1 ± 0.5	19.3 ± 0.1	7.0
10075-06	40.4 ± 0.2	19.8 ± 0.3	7.4 ± 0.1
Mean	41.1 ± 1.0	19.7 ± 0.7	6.6 ± 0.5
<i>Fines</i>			
10084-50	42.2 ± 0.5	20.4 ± 0.1	7.2 ± 0.2
10084-50	40.5 ± 0.9	20.3 ± 0.1	7.3 ± 0.1
10084-50	39.8 ± 0.5	20.0 ± 0.2	7.1 ± 0.1
Mean	40.8 ± 1.2	20.2 ± 0.2	7.2 ± 0.1

* Error limits for individual samples are standard deviations of the means calculated generally on the basis of 6 replicate analyses for Si and O and 2 replicate analyses for Al. Those for the means are standard deviations of individual rock abundances within each type.

replicate determinations were made. In the case of Al each value in Table 1 is the mean of duplicate determinations, except for rock 10074-05 which is just a single determination, and for the three aliquants of fines and rocks 10022-32 and 10073-21 where triplicate analyses were performed.

Table 2. Comparison of O, Si and Al analyses of Apollo 11 rocks and fines

N.A.S.A. No.	Oxygen (wt. %)	Silicon (wt. %)	Aluminum (wt. %)	Reference
<u>Type A</u>				
10022		18.7	4.6	a
	39.3	19.4	4.2	This work
<u>Type B</u>				
10003		17.7	5.8	a
		18.6	5.5	b
	38.1	17.9	5.1	This work
10024		18.2	5.0	a
		18.8	4.3	b
	38.9	18.5	4.1	This work
10047		19.3	5.2	a
	40.1	20.1	5.5	This work
10050		19.1	4.7	a
	40.5	18.4	5.3	This work
10058		19.5	6.2	a
		18.4	5.4	c
	39.9	19.0	5.5	This work
10062		18.1	6.4	a
		18.6	5.4	b
	38.0	18.0	5.3	This work
<u>Type C</u>				
10018		19.5	6.5	b
	40.7	19.6	6.1	d
	40.1	20.1	6.6	This work
10019		19.2	7.3	a
	39.9	18.9	6.5	This work
10048		19.7	6.8	a
	39.8	18.1	6.1	This work
10056		19.4	5.7	a
		19.8	5.7	c
	41.3	20.2	5.7	This work
10060		19.4	6.2	a
		18.7	6.0	c
	41.4	19.8	6.2	d
			5.2	e
		19.6	6.3	j
	40.3	20.0	6.2	This work
10061		19.6	6.7	b
	41.7	18.9	6.7	This work
<u>Fines</u>				
10084		19.5	7.1	b
		20.2	7.3	c
	41.5*	19.7	6.9	d
		20.1	7.0	e
		19.8	7.3	f
		19.7	7.4	g
	41.9	19.7	7.3	h
		19.4	7.6	i
		19.7	7.2	j
	40.8	20.2	7.2	This work
<u>Standard Rocks</u>				
BCR-1	45.5	25.5	7.2	k
	45.8	25.7	7.0	This work
K89	41.8†	18.1	5.3	l
	42.6‡			
	42.3	17.8	5.1	This work
VB-1	42.7	21.9	7.9	This work
VB-2	43.3	22.0	8.0	This work

A large number of analyses by several different methods is now available for the lunar rocks and soil, and some of these were made on rocks analyzed by us. Comparisons of analyses for rocks and fines are made in Table 2 and indicate no significant systematic bias. The accuracy of the O, Si and Al analyses of lunar rocks and soil was also checked by simultaneously analyzing BCR-1, NASA Knippa basalt K89, and NASA vesicular basalts VB-1 and VB-2. These results are given in the same table.

Our O results for the lunar rocks and fines appear to be lower than those obtained by WÄNKE *et al.* (1970) by about 0.5–1.0% O. Although this discrepancy is of the same order as our analytical uncertainty it is surprising that in all three cases where comparisons are possible our results are lower. In the past our O results on standard rocks have been marginally high by $\approx 0.3\%$ O (e.g. MORGAN and EHMANN, 1970) probably due to variable H_2O (LANGMYHR, 1970). As a result, very special care was taken to handle the lunar rocks and fines under high purity dry N_2 at all times to exclude the possibility of water contamination. It is suggested that our O analyses closely reflect the true abundance of O in the samples under lunar conditions.

DISCUSSION

(1) Chemical grouping of crystalline rocks

The crystalline rocks were classified by LSPET (1969) on the basis of crystal texture. COMPSTON *et al.* (1970) have defined two chemical groupings which do not correspond to the LSPET types. Group 1 is characterized by very high Rb, K, Ba and Th relative to Group 2. Of particular relevance to this discussion is the apparent depletion of Al in the Group 1 rocks. Of the specimens analyzed here, COMPSTON *et al.* classified 10022 and 10024 in Group 1 and 10003, 10047 and 10058 in Group 2. Of the remaining crystalline rocks listed in Table 2, 10069 and 10070 are clearly in Group 1 from the high Ba abundances (ANNEL and HELZ, 1970), and 10050 and 10062 can be ascribed to Group 2 on the basis of the low abundances of K (TUREKIAN and KHARKAR, 1970; ROSE *et al.*, 1970). For the crystalline rocks analyzed in this work

Refs. to Table 2:

- (a) ROSE *et al.* (1970). Si by SP; Al by CG and XRF.
- (b) COMPSTON *et al.* (1970). Si and Al by XRF.
- (c) MORRISON *et al.* (1970). Si by AA; Al by NA.
- (d) WÄNKE *et al.* (1970). O, Si and Al by NA.
- (e) SMALES *et al.* (1970). Si by XRF; Al by XRF and NA.
- (f) MAXWELL *et al.* (1970). Si and Al by CG and AA.
- (g) PECK and SMITH (1970). Si and Al by CG.
- (h) WIK and OJANPERÄ (1970). Si by CG and SP; Al by CG and AA.
O calculated by difference.
- (i) ENGEL and ENGEL (1970). Si and Al by CG.
- (j) AGRELL *et al.* (1970). Si and Al by CG.
- (k) FLANAGAN (1969).
- (l) Unpublished data provided by NASA.

* Sum of leach fractions yields 40.7%.

† O calculated from oxides scaled to 100%.

‡ O calculated by difference.

AA = atomic absorption; CG = classical gravimetry; NA = neutron activation;
SP = spectrophotometry; XRF = X-ray fluorescence.

the Al abundances in each group form a very narrow distribution. The four Group 1 rocks (10022-32; 10024-20; 10069-23; 10071-21) have a mean of 4.1 ± 0.2 and the five Group 2 rocks (10003-36; 10047-14; 10050-29; 10058-21; 10062-28) have a mean of 5.3 ± 0.2 . The means of the two groups are very significantly different ($t = 9.6$; $p < 0.01$) at the 95 per cent confidence level. Clearly the determination of Al by 14 MeV neutron activation as done in this work provides a ready method to characterize the crystalline rocks brought back by Apollo 11. The mean values of 39.0 ± 1.1 and $39.3 \pm 1.2\%$ O and 18.8 ± 0.5 and $18.7 \pm 0.9\%$ Si for Groups 1 and 2 respectively do not differ significantly ($t = 0.4$ and 0.3 , respectively).

(2) Breccias and fines

The mean values for O, Si and Al in the breccias are significantly higher (95 per cent confidence level) than for either group of crystalline rocks. Again, Al is very useful diagnostically, as the mean abundances in breccias and crystalline rocks differ very significantly, and there is a distinct hiatus between the two groups of values. The abundances of the three elements in the lunar fines closely resemble those found in certain breccias, for example 10073-21. However, because of the very small variance of the Al content of triplicate aliquants of fines, the difference between the mean Al values is significant at the 95 per cent confidence level ($t = 2.15$). It appears, that the breccias are not simply impacted soil, a conclusion reached independently from mineralogical evidence (DUKE *et al.*, 1970).

(3) Apparent oxygen deficiency

Several groups have reported high summations in total silicate analyses, particularly for the lunar fines (MAXWELL *et al.*, 1970; ROSE *et al.*, 1970; PECK and SMITH, 1970; WIK and OJANPERÄ, 1970). These apparent errors were ascribed to iron and/or titanium being more reduced than was assumed for the oxide calculations. ROSE *et al.* measured "total reducing capacity" chemically and expressed it as FeO. Iron values measured independently by X-ray fluorescence were then subtracted to give the "excess reducing capacity". This was found in all the samples analyzed, but was greatest in breccias, and particularly in fines. MAXWELL *et al.*, by a more direct method, found no anomaly in rock 10017 and only a small one in rock 10020. The fines, however, showed a large difference, equivalent to 1% FeO. An excess of reducing capacity of this size is too large to be due solely to metallic iron and MAXWELL *et al.* suspect the presence of Ti(III). ROSE *et al.* also checked total Fe in the fines chemically and arrived at 4.1% FeO excess reducing capacity. These discrepancies are difficult to resolve; however, MAXWELL *et al.* ground their samples to 100 mesh before analysis. Unless this was carried out under dry N₂ there is a very real possibility of oxidation (CHAO, 1963). ROSE *et al.* give no details of sample preparation. It should be noted, however, that ROSE *et al.* analyzed a fines sample (311079) different from that studied by MAXWELL *et al.* (10084-132).

Our data indicate that the O depletion of the original sample of fines 10084-50 may be even larger than this. It should be noted that our sample was quartered and packaged in a dry N₂ filled glove box. The mean O values for triplicate aliquants analyzed in our work show a rather large scatter. This is much larger than that found

using the same method on well-mixed powders (MORGAN and EHMANN, 1970), and probably reflects a real inhomogeneity. Grinding of the sample under dry N_2 and then splitting by quartering would probably have given more consistent results, however, this procedure was not permitted within the terms of our contract. The direct O mean for the soil is 40.8 per cent with a standard deviation for the mean (σ/\sqrt{n}) of $\pm 0.7\%$ O. The mean of three apparent abundances derived from chemical elemental analyses calculated as oxides (MAXWELL *et al.*, 1970; PECK and SMITH, 1970; WIK and OJANPERÄ, 1970) is 42.4 ± 0.1 per cent. The mean O depletion can be obtained from the difference between the direct and indirect determinations and is $1.6 \pm 0.7\%$ O. The high summations of the three total silicate analyses cited above indicate an O depletion of $0.6 \pm 0.0_3\%$. The difference between these two estimates of O depletion is not significant at the 95 per cent confidence level ($p \sim 0.3$).

It is interesting to speculate upon the cause of the apparently smaller O depletion observed in the crystalline rocks when compared to the breccias and particularly the fines. The work of MAXWELL *et al.* (1970) indicates that the O depletion in the crystalline rocks is minimal or possibly even non-existent. The high abundance of solar wind rare gases in the fines and breccias (LSPET, 1969) suggest the possibility that some reduction could take place by solar wind H. Assuming a solar wind origin for the Xe in fines and breccias (LSPET, 1969), it is possible to calculate from the relative solar abundances of H and Xe that more than sufficient solar wind H has impinged upon the soil and breccias to combine with all the O in these materials. On the other hand, a similar calculation shows that solar wind H could *at best* only reduce about 1 or 2 per cent of the O in the crystalline rocks.

(4) Oxygen in the moon, earth and meteorites

In order to compare the O abundances found in the lunar rocks and fines with terrestrial and meteoritic abundances, in Fig. 1 we have plotted O against Si abundance (EUGSTER, 1969). Meteorite abundances are taken from VOGT and EHMANN (1965a, b). Because of the problem of terrestrial oxidation, only chondrite analyses for *falls* have been used. In terrestrial rocks (EUGSTER, 1969), Si and O are correlated and can be expressed as:

$$\% O = 0.415\% Si + 35.0. \quad (1)$$

Terrestrial abundances in Fig. 1 are represented by a line based on equation 1. A regression line calculated for lunar rocks can be written as:

$$\% O = 1.15\% Si + 18.2. \quad (2)$$

The lunar fines do not follow this regression, and show a variation of O abundance for almost constant Si. The ordinary chondrites lie on the lunar rock regression, although the O and Si abundances within the H or L group chondrites are not correlated. When the values for 13 H and L group chondrites are introduced into the lunar rock regression they cause no significant change in slope (1.11) or intercept

(18-6). The low O/Si ratio in the ordinary chondrites is due to the presence of FeS and Fe-Ni but in the lunar rocks the presence of significant amounts of ilmenite (31-6% O) and of Ti(III) is largely responsible.

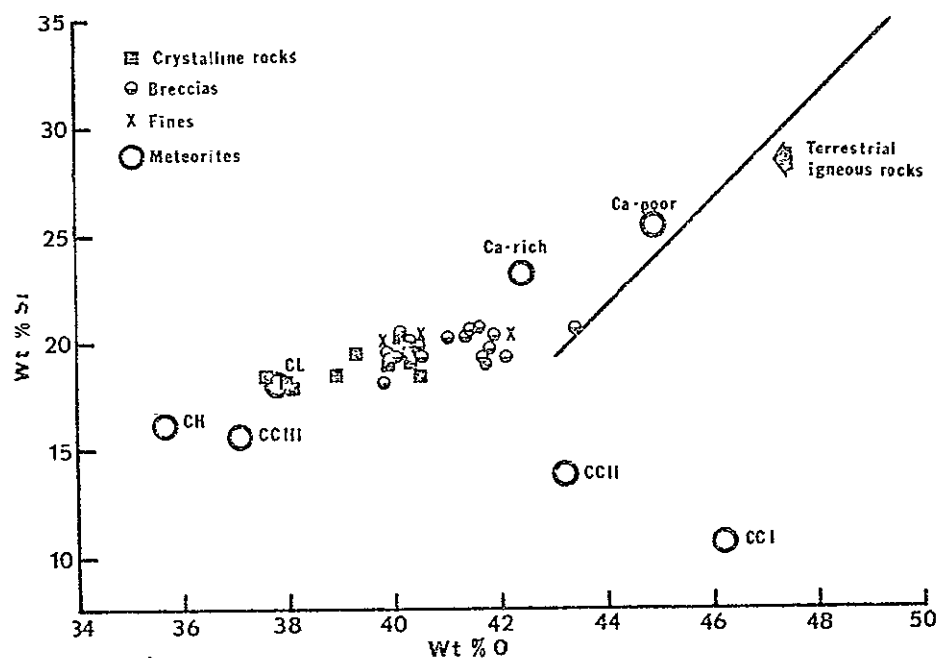


Fig. 1. Relation of Si and O in lunar rocks. The line for terrestrial igneous rocks is based on that derived by EUGSTER (1969). Large circles represent stony meteorite averages, where Ca-rich and Ca-poor refer to the appropriate achondrites, CCI, II and III represent carbonaceous chondrite types and CH and CL are H and L group chondrites respectively.

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SECTION VI

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Elemental abundances by instrumental activation analyses in chips from 27 lunar rocks

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Abstract—Analyses of 27 chips from lunar rocks by instrumental activation techniques provided data on Si, Ti, Al, Fe, Mg, Ca, O, Na, Ba, La, Ce, Sm, Eu, Tb, Ho, Yb, Lu, U, Zr, Hf, Ta, Mn, Cu, Co, Sc, V and Cr. These abundances may be used to comment on the merits of various analytical methods and to survey geochemical characteristics of Apollo 11 rocks. We propose on compositional grounds that rocks 10024 and 10071 should be classified as "basalts" rather than as "microgabbros". The "microgabbro" 10050 is compositionally anomalous, with low Fe (in which it resembles breccias), about 6.5% Mg which is the highest Mg content we have measured in these materials, and low La and Hf contents. It may be a specimen from a geologic unit distinct from that on which Eagle landed. Breccia 10056 is also compositionally anomalous, but it resembles "microgabbros" like 10047 closely enough so that one need not adduce exotic provenance as an explanation.

TWENTY-SEVEN chips from diverse rocks of the Apollo 11 collection were provided for analysis by our instrumental activation techniques. Three purposes were served by this work: (1) A library of specimens for which many elemental abundances are known is made available for further, possibly grossly destructive, investigations. Our work leaves minute amounts of artificially-induced long-lived radioactivities in the specimens and introduces minor radiation damage, principally from fast-neutron bombardment, but the specimens are physically intact and essentially unmodified chemically. (2) We gain experience in comprehensive analyses of gram-sized specimens, in case it ever becomes necessary to undertake elaborate sequential investigations of especially rare materials. (3) We learn much about the geochemistry of a wide variety of Apollo 11 rocks. This paper is mainly concerned with the first and second of these aims; we here discuss briefly some technical innovations, report our data, and compare them with abundances determined by other workers. Geochemical interpretations of the data are in large part reserved for other papers in this issue.

Of the rock chips, four are "basalts", five are "microgabbros" and the remainder are breccias. Two of the "basalts", 10024 and 10071, were initially classified as Type B rocks or "microgabbros" (WARNER, personal communication). We consider them to be "basalts" on compositional grounds, but detailed petrographic studies should be undertaken to clarify their classification.

Data on Si, O and one set of Al abundances were obtained by two of us (W.D.E. and J.W.M.) using 14-MeV neutron activation analysis as described by MORGAN and

EHMANN (1970). Samples and standards were packaged for irradiation and counting under a dry nitrogen atmosphere in the manner of EHMANN and MCKOWN (1968). Silicon and oxygen abundance estimates are based on 5–12 replicate analyses of each specimen, yielding standard deviations from the mean of about $\pm 0.12\%$ Si and $\pm 0.29\%$ O. Aluminum abundance estimates are based on only two analyses (for the EHMANN-MORGAN data set) of each specimen, which yield an average deviation from the mean of $\pm 0.2\%$ Al.

Data on Ti, Al (the second set), Mg, Ca, Na, Mn, Cu and V were obtained by the Oregon State University group (R.A.S. and H.W., with some assistance from their co-workers). A brief account of the activation levels, nuclear reactions and detectors employed is given in this issue (WAKITA *et al.*, 1970). A more detailed description is given by SCHMITT *et al.* (1970). During photonuclear activation (with 23-MeV bremsstrahlung) for determination of Mg, which was done at the electron linear accelerator of Gulf General Atomic, San Diego, the vial containing specimen 10050-29 ruptured. Modifications of the method of EHMANN and MCKOWN have been devised to obviate this problem, which arises because of the large decelerations experienced by the specimen container in the "catcher" of the electron linear accelerator.

Table 1. Major elements in igneous rocks (wt. %)

	"Basalts"				"Microgabbros"					Range in error esti- mates
	10022-32	10069-23	10024-20	10071-21	10003-36	10047-14	10058-21	10062-28	10050-29	
Si	19.4	18.3	18.5	19.1	17.9	20.1	19.0	18.0	18.4	0.1-0.2
Ti	7.1	7.2	7.5	7.0	7.1	6.0	6.1	6.7	6.6	0.3-0.4
Al*	4.2	3.7	4.1	4.2	5.1	5.5	5.5	5.3	5.3	0.2-0.3
	4.7	3.8	4.3	4.5	5.7	5.7	6.3	6.1	5.8	0.1-0.2
Fe	15.7	14.1	15.4	14.9	15.3	15.1	14.9	15.0	13.6	0.2-0.4
Mg	4.1	3.7	4.3	4.4	4.9	3.5	3.8	—	6.5	0.2-0.4
Ca	7.4	7.1	7.1	7.2	8.3	8.7	8.1	9.3	8.2	0.7-0.9
O	39.3	37.6	38.9	40.3	38.1	40.1	39.9	38.0	40.5	0.1-0.5

* First set of values for Al are those determined by W.D.E. and J.W.M. The second set (single determinations only) were done by R.A.S. and H.W.

Table 2. Major elements in breccias (wt. %)

	10018-21	10019-11	10021-22	10048-32	10056-23	10059-30	10060-17	10061-32	10063-05	10064-10	Range in error estimates
Si	20.1	18.9	19.6	18.1	20.2	19.1	20.0	18.9	20.3	19.4	0.1–0.2
Ti	4.9	4.9	4.9	4.8	5.8	4.7	5.1	4.4	5.3	5.6	0.2–0.3
Al*	6.6	6.5	6.7	6.1	5.7	6.4	6.2	6.7	6.6	5.9	0.2
	7.7	7.5	7.2	6.7	6.4	7.0	6.0	7.8	7.7	5.6	0.2–0.3
Fe	13.1	12.7	13.1	13.2	14.8	12.9	13.1	12.63	13.1	12.8	0.18–0.4
Mg	5.1	3.8	5.0	4.1	3.9	5.1	4.9	5.9	4.7	4.3	0.2–0.5
Ca	8.8	9.0	7.7	8.0	9.4	8.1	—	—	9.7	—	0.8–1.0
O	40.1	39.9	41.8	39.8	41.3	40.0	40.3	41.7	41.9	40.5	0.1–0.6

	10065-14	10066-05	10067-05	10068-20	10070-05	10073-21	10074-05	10075-06	Range in error estimates	
Si	19.3	20.2	20.6	19.3	20.6	20.5	19.3	19.8	0.1–0.3	
Ti	4.7	4.9	5.3	4.7	5.0	4.9	4.7	4.5	0.2–0.3	
Al*	6.6	6.9	7.0	6.3	7.1	7.3	7.0	7.4	0.2	
	6.6	7.8	8.1	6.8	7.8	7.7	9.3	8.7	0.2–0.3	
Fe	13.1	12.8	13.9	12.8	12.6	12.6	11.9	12.1	0.2–0.3	
Mg	5.0	4.6	7.2	3.9	5.2	4.7	4.1	4.7	0.2–0.4	
Ca	9.4	8.6	8.7	8.7	8.8	8.9	9.3	8.5	0.8–0.9	
O	41.6	41.0	41.6	40.3	43.4	41.4	42.1	40.4	0.1–0.7	

* First set of values for Al are those determined by W.D.E. and J.W.M. The second set (single determinations only) were done by R.A.S. and H.W.

Data on Fe, Ba, La, Ce, Sm, Eu, Tb, Ho, Yb, Lu, U, Zr, Hf, Ta, Co, Sc and Cr were obtained by the University of Oregon group (G.G.G., K.R. and M.O., with much assistance from their co-workers). These abundances were determined by techniques similar to those of GORDON *et al.* (1968). A noteworthy extension of the previous techniques is the determination of U according to AMIEL's (1962) method, but using an array of fourteen BF_3 neutron detectors.

Elemental abundances and error estimates are presented in Tables 1-4. Errors cited are estimates of single standard deviations; owing to editorial policy, only ranges are given. Major elements in Tables 1 and 2 are presented in the conventional order, with O last; minor and trace elements in Tables 3 and 4 are listed in the order suggested by TAYLOR (1965). The complete Lunar Receiving Laboratory specimen designation is given only in Tables 1 and 2. The igneous rocks which seem in some way anomalous ("basalts" 10024 and 10071, "microgabbro" 10050) are listed out of numerical order to emphasize their peculiar character. Although some of the breccias (notably 10056) may also be compositionally anomalous, we do not feel confident enough of their distinct character to place them in a separate subgroup.

Averages of major element abundances are compared in Table 5. Where necessary, we have reclassified rocks to conform to the scheme used in this paper. It is apparent from Table 5 that the degree of agreement between estimates of bulk composition obtained by different workers is very satisfactory. Almost all differences may be accounted for by sampling rather than analytical problems. Perhaps TUREKIAN and KHARKAR (1970) are systematically too low for Ti, and the Ca values of MORRISON *et al.* (1970) seem to be too high. There is a systematic difference between the two sets of Al abundances reported in this paper, which of course cannot be related to sampling difficulties, but it is not yet clear which set should be considered the more reliable one. In any case, a reasonable inference from the data of Table 5 is that our instrumental techniques are fully competitive with more-conventional rock analysis methods.

Owing to sampling problems and possible marked heterogeneity from one rock to another within a given class, we have not averaged minor- and trace-element abundances for purposes of making comparisons. Rather, Table 6 presents for comparison various sets of determinations of elements in different samples of selected rocks. Rocks were chosen for inclusion in Table 6 on the basis of having extensive data sets available, with a secondary consideration that of providing a representative selection. Agreement between the results in Table 6 is gratifying, especially to one who recalls problems associated with securing agreement among analyses of standard rocks such as G-1 and W-1 in diverse laboratories. Some of the disagreements exhibited in Table 6 may be related to sampling but others seem to arise from serious analytical errors. We comment below on both types of disagreements, on an element-by-element basis.

General agreement among Na abundances is good, although the LSPET (1969) values scatter rather widely and the values reported by ROSE *et al.* (1970) are systematically too high by about a factor two. For rocks of these compositions, the instrumental activation analysis technique for Na is clearly one of the best available (see also SCHMITT *et al.*, 1965; and STUEBER and GOLEŠ, 1967).

In contrast, our method for determination of Ba is of marginal utility. It is not certain whether this element is quite heterogeneously distributed in these rocks or whether the accuracies and precisions implied by other workers are overoptimistic. Two isotope dilution results for Ba in rock 10058 differ by about 6 per cent of their

Table 3. Minor and trace elements in igneous rocks (ppm)

	"Basalts"				"Microgabbros"					Range in error esti- mates
	10022	10069	10024	10071	10003	10047	10058	10062	10050	
Na	3550	3650	3620	3640	2700	3490	3020	3140	2630	50-70
Ba	220	250	170	450	220	—	140	230	—	50-80
La	25.9	23.7	23.0	25.8	13.5	11.3	11.8	13.1	7.2	0.3-0.5
Ce	81	65	76	84	37	46	39	38	34	2-3
Sm	20.3	18.0	19.2	20.0	13.0	18.9	14.0	11.9	11.8	0.2-0.3
Eu	2.15	2.04	—	2.12	1.84	2.71	2.14	2.07	2.0	0.08-0.2
Tb	5.7	4.8	—	5.7	3.5	4.1	3.5	3.3	2.1	0.2-0.6
Ho	8.2	6.9	8.1	9.2	4.0	7.9	5.5	4.4	4.6	0.4-0.9
Yb	21	20.8	19.6	20.8	15.3	18.2	14.0	13.5	11.1	0.5-3
Lu	2.69	2.67	3.20	3.08	2.62	2.88	1.94	1.94	1.96	0.05- 0.12
U	0.67	0.78	0.67	0.69	0.31	0.16	0.18	0.27	0.21	0.04- 0.10
Zr	130	520	650	210	560	—	190	290	—	80-160
Hf	19.6	17.8	20.0	19.1	11.6	13.2	11.2	11.8	8.6	0.3-1.0
Ta	1.8	2.7	2.4	2.0	—	2.6	1.6	1.0	2.2	0.3-0.5
Mn	1770	1600	1640	1650	1740	2100	1870	1790	1990	100-120
Cu	—	12	—	11	—	—	—	—	—	2
Co	29.8	26.0	28.4	27.1	14.1	12.2	14.4	13.8	13.6	0.4-0.7
Sc	76.6	72.4	76.2	73.2	74.0	92.0	80.8	74.7	88.9	0.8-1.1
V	89	87	84	92	63	63	78	75	117	6-10
Cr	2250	2130	2290	2170	1390	1250	1800	1540	2120	30-100

Table 4. Minor and trace

	10018	10019	10021	10048	10056	10059	10060	10061	10063
Na	3720	3530	3430	3490	3370	3590	3630	3550	3380
Ba	280	—	350	200	240	—	—	260	—
La	16.9	15.5	17.5	17.3	11.0	18.1	17.7	16.8	16.7
Ce	61	54	61	38.1	34	59	61	48.6	—
Sm	14.6	12.7	15.0	13.2	17.8	15.1	15.4	13.2	12.9
Eu	1.82	1.78	1.80	1.91	2.63	1.78	1.84	1.78	1.83
Tb	3.6	—	4.2	3.8	5.0	3.7	3.7	3.4	—
Ho	5.3	5.0	6.9	4.6	6.5	5.5	5.3	3.7	4.7
Yb	15.2	11.7	14.5	15.2	18.0	12.5	13.2	13.1	11.0
Lu	2.14	1.84	2.25	1.90	2.5	1.97	2.30	1.94	1.76
U	0.60	0.49	0.56	0.69	0.18	0.52	0.51	0.59	0.51
Zr	340	580	250	240	340	—	770	240	490
Hf	12.9	10.8	12.2	14.5	13.8	11.5	12.1	13.1	13.1
Ta	1.4	1.7	1.6	1.9	1.6	1.6	2.1	—	—
Mn	1590	1510	1560	1560	1970	1440	1650	1450	1620
Cu	—	—	—	—	—	—	—	—	16
Co	32.7	34.5	30.7	32.2	11.9	34.0	31.6	33.7	35.2
Sc	60.3	60.9	61.8	62.7	91.6	61.1	64.0	59.6	62.2
V	67	63	73	67	47	64	58	80	90
Cr	1880	1870	1950	1950	1280	1900	1880	1930	1940

mean value (GAST and HUBBARD, 1970; and MURTHY *et al.*, 1970), but two isotope dilution results for another "microgabbro", 10062, differ by about 50 per cent of their mean value (GAST and HUBBARD, 1970; and PHILPOTTS and SCHNETZLER, 1970). Some of our values agree well with isotope dilution results, but others seem to lie as much as two standard deviations above them (see data for 10071, 10003, 10062 and 10021).

The degree of agreement among rare earth abundances is extraordinary. Cerium abundances appear to reflect sampling or analytical difficulties, even if one considers only activation analysis or isotope dilution results, but these do not obscure fundamental differences between specimens. Samarium abundances of MORRISON *et al.* (1970) seem to be systematically too high, and those of WÄNKE *et al.* (1970) too low, but these characteristics are discernible only against a background of excellent agreement in other data. Terbium presents analytical difficulties to the activation analyst and much of the scatter in abundances of this element may be related to them. Holmium data are sparse, but perhaps the values of MORRISON *et al.* are too high. LSPET (1969) values for Yb are certainly much too low, as seem to be (to a lesser degree) those of TUREKIAN and KHARKAR (1970). Two out of the three values for Yb by MORRISON *et al.* seem to be too high. Excluding these data, Yb abundances suggest that this element is rather homogeneously distributed in these rocks. Our Lu values may be systematically too high, and those of TUREKIAN and KHARKAR are too low.

Most of the Zr values reported by LSPET (1969) are clearly too high, but even upon excluding these data much scatter remains. ROSE *et al.* (1970) may have overestimated their sensitivity for this element, but in any case they were working close to their detection limit. In view of the significance which abundances of this element are likely to have for questions of lunar petrogenesis (GOLEŠ *et al.*, 1970), it would be

elements in breccias (ppm)

10064	10065	10066	10067	10068	10070	10073	10074	10075	Range in error estimates
3650	3600	3420	3590	3280	3740	3220	3750	3350	60-180
290	220	—	—	150	310	—	280	430	50-100
19.6	17.8	17.4	20.1	16.4	17.3	12.8	13.8	14.9	0.3-0.4
59	63	62	68	60	56	48	55	50	1.7-5
15.5	14.6	15.1	16.7	14.4	13.1	11.5	11.5	11.5	0.2-0.3
1.77	1.73	1.70	2.4	1.80	1.74	1.60	1.73	1.62	0.07-0.2
3.7	4.0	2.8	3.1	3.6	3.1	—	2.8	3.1	0.3-0.5
5.5	6.7	6.5	7.5	6.6	5.8	5.0	5.0	5.4	0.4-0.8
14.8	14.5	11.8	13.8	12.2	14	7.2	12	11.2	0.4-1.5
2.46	2.01	1.90	2.20	2.6	1.80	1.76	1.7	1.89	0.06-0.15
0.65	0.54	0.56	0.54	0.61	0.62	0.45	0.49	0.52	0.05-0.08
520	—	—	—	700	360	—	500	390	70-180
13.9	12.1	10.6	15.4	11.0	12.8	8.9	11.9	8.8	0.3-0.5
1.7	2.1	2.1	2.1	1.8	1.0	1.6	1.0	1.4	0.3-0.4
1600	1540	1590	1820	1470	1520	1580	1420	1540	80-110
—	—	—	—	15	12	14	10	10	2
29.0	31.6	33.8	35.9	31.7	37.3	31.1	30.9	28.7	0.4-0.9
60.5	62.6	60.3	66.0	60.9	57.4	62.0	53.7	56.8	0.6-1.6
73	84	59	71	46	82	82	78	85	6-17
1850	1890	1910	2040	1890	1860	1900	1770	1790	50-80

Table 5A. Averages of major-element abundances in "basalts" (wt. %)

	Si	Ti	Al	Fe	Mg	Ca	O
This work (4 rocks)	18.8 ± 0.5	7.2 ± 0.2	4.1 ± 0.2* 4.3 ± 0.4†	15.0 ± 0.7	4.1 ± 0.3	7.2 ± 0.1	39.0 ± 1.1
COMPSTON <i>et al.</i> (1970) (3 rocks)	18.9	7.2	4.2	15.1	4.5	7.6	—
GAST and HUBBARD (1970) (3 rocks)	—	7.6	—	—	—	7.5	—
MORRISON <i>et al.</i> (1970) (3 rocks)	20.0	6.4	4.6	15.3	4.3	10.2	—
ROSE <i>et al.</i> (1970) (2 rocks)	18.7	7.6	4.8	14.5	4.8	7.4	—
TAYLOR <i>et al.</i> (1970) (7 rocks)	19.3	6.5	5.2	14.2	4.6	7.5	—
WÄNKE <i>et al.</i> (1970) (2 rocks)	19.3	6.8	4.2	14.3	4.5	8.3	40.6

Table 5B. Averages of major-element abundances in "microgabbros" (wt. %)

	Si	Ti	Al	Fe	Mg	Ca	O
This work (5 rocks)	18.7 ± 0.9	6.5 ± 0.5	5.3 ± 0.2* 5.9 ± 0.9†	14.8 ± 0.7	4.7 ± 1.4	8.5 ± 0.5	39.5 ± 1.1
COMPSTON <i>et al.</i> (1970) (4 rocks)	18.8	6.3	5.3	15.1	4.1	8.2	—
GAST and HUBBARD (1970) (4 rocks)	—	5.8	—	—	—	7.9	—
ROSE <i>et al.</i> (1970) (6 rocks)	18.8	6.6	5.6	14.5	4.2	8.1	—
TAYLOR <i>et al.</i> (1970) (8 rocks)	19.0	5.5	6.2	14.0	4.8	7.6	—
TUREKIAN and KHARKAR (1970) (2 rocks)	—	3.8	—	12.5	—	—	—

Table 5C. Averages of major-element abundances in breccias (wt. %)

	Si	Ti	Al	Fe	Mg	Ca	O
This work (18 rocks)	19.7 ± 0.7	5.0 ± 0.4	6.6 ± 0.5* 7.4 ± 0.9†	13.0 ± 0.6	4.6 ± 0.6	8.8 ± 0.6	41.1 ± 1.0
COMPSTON <i>et al.</i> (1970) (2 rocks)	19.5	4.7	6.6	12.8	4.7	8.6	—
MORRISON <i>et al.</i> (1970) (3 rocks)	19.7	5.2	6.0	13.9	4.3	10.4	—
ROSE <i>et al.</i> (1970) (4 rocks)	19.4	5.6	6.5	12.7	4.4	8.4	—
TAYLOR <i>et al.</i> (1970) (3 rocks)	19.6	5.3	6.2	13.7	5.1	7.4	—
TUREKIAN and KHARKAR (1970) (2 rocks)	—	3.8	—	12.5	—	—	—
WÄNKE <i>et al.</i> (1970) (2 rocks)	19.7	5.1	6.2	11.6	4.8	—	41.1

* Determined by W.D.E. and J.W.M.

† Determined by R.A.S. and H.W. Single determinations only.

worthwhile to undertake a detailed investigation of its distribution by, e.g. isotope dilution or radiochemical activation techniques. An efficient way to attack this problem would be to use some of the chips reported on here, for which accurate Hf data are already available with which to construct Zr/Hf ratios.

Activation analysis determinations of Mn seem to be more reliable than any of the various spectrographic or X-ray fluorescence results. The relatively subtle differences from one rock to another in Mn contents probably are best mapped with our technique.

LSPET (1969) values for Co are too low; otherwise the agreement for this element is good.

Scandium values reported by LSPET tend to scatter in an apparently unrealistic way. Our Sc results are systematically slightly lower than those of other activation analysts or of ANNEEL and HELZ (1970); since we used standard rock W-1 as a flux monitor for this element, it is not easy to rationalize this disagreement.

LSPET values for V are too low, but in several cases might represent the lower end of the actual range of abundances in small samples. Without more information, it is not possible to decide whether we are faced with sampling or analytical problems for this element.

Agreement among Cr abundances is unsatisfactory, even if one focusses on activation analysis results alone. For example, four determinations of Cr in breccia 10060 by activation techniques are: 1880 ± 60 , 2200, 2800 and 1820 (all in ppm). It seems likely that there are severe sampling problems here, and that all results (with the possible exception of those by LSPET) are equally valid from an analytical standpoint.

We shall conclude by discussing briefly the evidence for geochemical clans among these rocks. As has been pointed out by numerous investigators at the Apollo 11 Conference, there are first-order distinctions between igneous rocks and clastic materials (breccias and "soil"). We can now discern second-order distinctions within these classes, exhibited in abundances of many elements. Consider Tables 1 and 2, especially data for Ti, Al and Ca. Titanium is relatively high in "basalts" and, on the average, intermediate in "microgabbros" and low in breccias. Aluminum is distributed in a mirror-image way (EHMANN and MORGAN, 1970), as is Ca, although less strikingly. In phratry A, the "basalts", there is no chemical distinction between clan A-1, rocks 10022 and 10069 whose classification was never in doubt, and clan A-2, rocks 10024 and 10071. (This statement is valid for the data of Table 3 as well.) In phratry B, "microgabbros" fall into two clans, the populous B-1 (10003, 10047, 10058, 10062) and the apparently rare B-2 clan of rock 10050. Rock 10050 is chemically very unusual, with low Fe (near the upper end of the breccia range), the highest Mg content we have measured, and strikingly-low La and Hf contents. It does not seem likely that it can be petrogenetically related in a simple way to the other "microgabbros".

Among the breccias of phratry C, we may pick out a C-2 clan consisting only of rock 10056. This rock has a Ti content like those of the B-1 clan, rather low Al, and the highest Fe content among the breccias. Its trace-element abundances resemble very closely those of "microgabbro" 10047. Presumably our sample of 10056 contains one or more clasts of rocks of clan B-1 which tend to dominate the geochemical relationships. Perhaps one cannot even exclude mislabeling as an explanation of these observations. Our chip (10056-23) appears on superficial examination to be a

Table 6. Comparisons of minor and trace elemental

	10022	10071	10003	10058	10062
Na	3550 \pm 70 3000 ^f 6700 ^f	3640 \pm 70 3900 ^c	2700 \pm 60 3000 ^b 2900 ^c 6300 ^l	3020 \pm 60 2900 ^c 4100 ^f 3200 ^g 5000 ^l 2990 ^p	3140 \pm 60 3000 ^b 3300 ^c 5100 ^l 2990 ^p
Ba	220 \pm 70 100 ^f 277 ^h	450 \pm 80 470 ^a 327 ^c	220 \pm 60 160 ^a 108 ^c	140 \pm 70 117 ^c 85 ^f 140 ^g 124 ^h	230 \pm 70 79 9 ^c 134 ^k
La	25 9 \pm 0 5 26 4 \pm 0 7 ^d	25 8 \pm 0 4 27 ^a 27 8 ^c	13 5 \pm 0 3 15 ^a 15 1 ^c 14 1 \pm 0 2 ^d	11 8 \pm 0 3 11 7 ^c 16 ^g	13 1 \pm 0 3 13 8 ^c 12 ^p
Ce	81 \pm 2 68 \pm 2 ^d	84 \pm 2 83 5 ^c	37 \pm 2 47 2 ^c 41 3 \pm 0 7 ^d	39 \pm 2 40 2 ^c 45 ^g	38 \pm 2 42 7 ^c 40 2 ^k 48 ^p
Sm	20 3 \pm 0 3 21 2 \pm 0 1 ^d	20 0 \pm 0 3 22 7 ^c	13 0 \pm 0 2 14 5 ^c 13 1 \pm 0 1 ^d	14 0 \pm 0 2 17 1 ^c 22 ^g	11 9 \pm 0 2 13 3 ^c 14 7 ^k 10 ^p
Eu	2 15 \pm 0 10 2 04 \pm 0 01 ^d	2 12 \pm 0 15 2 29 ^c	1 84 \pm 0 09 1 82 ^c 1 80 \pm 0 01 ^d	2 14 \pm 0 11 2 64 ^c 3 0 ^g	2 07 \pm 0 08 2 02 ^c 2 07 ^k 1 8 ^p
Tb	5 7 \pm 0 6 4 7 \pm 0 1 ^d	—	3 5 \pm 0 3 3 26 \pm 0 07 ^d	3 5 \pm 0 2 5 4 ^g	—
Ho	8 2 \pm 0 8 5 5–8 7 ^d	—	4 0 \pm 0 6 3 7–4 4 ^d	5 5 \pm 0 5 9 ^g	—
Yb	21 \pm 3 17 7 \pm 0 5 ^d 7 ^f	20 8 \pm 1 6 20 2 ^c	15 3 \pm 0 7 12 7 ^c 11 9 \pm 0 3 ^d	14 0 \pm 1 3 15 2 ^c 5 ^f 22 ^g	13 5 \pm 1 3 12 1 ^c 11 3 ^k 6 3 ^p
Lu	2 69 \pm 0 09 2 55 \pm 0 02 ^d	3 08 \pm 0 07 2 87 ^c	2 62 \pm 0 08 1 81 ^c 1 69 \pm 0 01 ^d	1 94 \pm 0 08 2 14 ^c 2 3 ^g	1 94 \pm 0 07 1 73 ^c 1 76 ^k 0 87 ^p
U	—	0 69 \pm 0 09 0 873 ^o	0 31 \pm 0 05 0 26 \pm 0 03 ^l 0 29 \pm 0 02 ^j 0 268 ^o	0 18 \pm 0 05 0 20 ^g	—
Zr	130 \pm 110 1000 ^f ~200 ^l	210 \pm 110 644 ^a	560 \pm 160 380 ^a 309 ^b <200 ^l	190 \pm 100 250 ^f 380 ^g <200 ^l	290 \pm 80 319 ^b <200 ^l
Hf	—	—	—	11 2 \pm 0 4 13 ^g	11 8 \pm 0 3 10 ^p

Elemental abundances by instrumental activation analyses in chips from 27 lunar rocks 1173

abundances in selected individual rocks (ppm)

10050	10018	10021	10056	10060	10061
2630 ± 50 3800 ^f 4900 ^l	3720 ± 180 3400 ^b 3920 ^q	3430 ± 70 1500 ^f 3470 ^p	3370 ± 60 3200 ^g	3630 ± 70 3400 ^g 5800 ^l 3800 ⁿ 3600 ^q	3550 ± 70 3500 ^b 3700 ^f
—	280 ± 70 220 ^a 175 ^b 200 ^k	350 ± 80 270 ^a 105 ^f 211 ^k	240 ± 80 100 ^g	—	260 ± 70 270 ^a 128 ^b 90 ^f
—	16.9 ± 0.4 15 ^a 24 ^b 18 ^q	17.5 ± 0.4 22 ^a	11.0 ± 0.3 13 ^g 12 ^p	17.7 ± 0.4 20.8 ± 0.4 ^d 25 ^a 18 ^q	16.8 ± 0.4 18 ^a 23 ^b
—	61 ± 2 67 ^b 52.8 ^k	61 ± 2 57.2 ^k	34 ± 2 42 ^g 75 ^p	61 ± 3 58 ± 1 ^d 62 ^g 59.0 ^k 56 ⁿ	48.6 ± 1.9 37 ^b
—	14.6 ± 0.3 16.3 ^k 8.5 ^q	15.0 ± 0.2 17.2 ^k 12 ^p	17.8 ± 0.3 23 ^g 17 ^p	15.4 ± 0.3 15.4 ± 0.1 ^d 24 ^g 17.5 ^k 16 ⁿ 8.7 ^q	—
—	1.82 ± 0.09 1.84 ^k 1.68 ^q	1.80 ± 0.09 1.91 ^k 1.8 ^p	2.63 ± 0.16 2.5 ^g 2.9 ^p	1.84 ± 0.08 2.06 ± 0.02 ^d 2.0 ^g 1.98 ^k 1.9, 2.6 ⁿ 1.61 ^q	—
—	—	—	5.0 ± 0.5 5.4 ^g	3.7 ± 0.4 3.6 ± 0.1 ^d 5.0 ^g 6 ⁿ	—
—	—	—	6.5 ± 0.8 9 ^g	5.3 ± 0.6 4.4–5.4 ^d 10 ^g 7 ⁿ	—
11.1 ± 0.5 2.7 ^f	15.2 ± 0.4 11.8 ^k 11.1 ^q	14.5 ± 0.7 4.5 ^f 12.7 ^k	18.0 ± 1.5 20 ^g 8.3 ^p	13.2 ± 0.7 13.2 ± 0.3 ^d 22 ^g 12.7 ^k 14 ⁿ 10.9 ^q	13.1 ± 0.5 1.8 ^f
—	2.14 ± 0.07 1.87 ^k 1.56 ^q	2.25 ± 0.07 1.99 ^k	2.5 ± 0.3 1.8 ^g 1.2 ^p	2.30 ± 0.08 2.00 ± 0.02 ^d 2.0 ^g 1.92 ^k 1.8 ⁿ 1.57 ^q	—
0.21 ± 0.05 0.156 ^o	0.60 ± 0.08 0.60 ± 0.09 ^f	0.56 ± 0.09 0.54 ± 0.08 ^f 0.39 ^p	0.18 ± 0.05 0.21 ^g 0.45 ^p	0.51 ± 0.07 0.60 ^g 0.60 ^m 0.4 ⁿ	0.59 ± 0.08 0.674 ^o
— 700 ^f <200 ^f	340 ± 100 429 ^a 328 ^b	250 ± 90 424 ⁿ 1500 ^f	340 ± 110 410 ^g	770 ± 110 580 ^g ~300 ^f 300, 320, 340 ⁿ	240 ± 70 393 ^a 342 ^b 400 ^f
—	—	—	13.8 ± 0.5 11 ^g 11 ^p	13.1 ± 0.3 13 ^g 12 ⁿ	—

Table 6 (continued). Comparisons of minor and trace

	10022	10071	10003	10058	10062
Ta	—	—	—	1.6 ± 0.3 1.0 ^f	1.0 ± 0.3 1.8 ^p
Mn	1770 ± 110 2000 ^f 1900 ⁱ	1650 ± 100 2230 ^a	1740 ± 100 2580 ^a 2300 ^b 2200 ⁱ	1870 ± 110 4300 ^f 1900 ^g 2100 ⁱ	1790 ± 110 2300 ^b 2100 ⁱ 1510 ^p
Co	29.8 ± 0.7 15 ^f	27.1 ± 0.7 33 ^a	14.1 ± 0.4 15 ^a	14.4 ± 0.4 7 ^f 14 ^g	13.8 ± 0.4 13 ^p .
Sc	76.6 ± 1.0 110 ^f	73.2 ± 1.0 97 ^a	74.0 ± 0.8 94 ^a	80.8 ± 1.1 130 ^f 87 ^g	74.7 ± 0.8 76 ^p
V	89 ± 8 36 ^f	92 ± 9 78 ^a	63 ± 7 82 ^a	78 ± 9 32 ^f 41 ^g	—
Cr	2250 ± 100 2800 ^f 2500 ⁱ	2170 ± 80 3060 ^a	1390 ± 30 1860 ^a 1800 ⁱ	1800 ± 70 3700 ^f 1500 ^g 1600 ⁱ	1540 ± 40 1700 ^f 1310 ^p

a. ANNEL and HELZ (1970); emission spectrography.

b. COMPTON *et al.* (1970); X-ray fluorescence, flame photometry.

c. GAST and HUBBARD (1970); isotope dilution, atomic absorption, X-ray fluorescence, wet chemical

d. HASKIN *et al.* (1970); radiochemical activation analysis.e. KEAYS *et al.* (1970); radiochemical activation analysis.

f. LSPET (1969); principally emission spectrography.

g. MORRISON *et al.* (1970); activation analysis and spark-source mass spectrography.h. MURTHY *et al.* (1970); isotope dilution.i. O'KELLEY *et al.* (1970); gamma-ray spectrometry.

single clast of an intensely microbrecciated, relatively coarse-grained igneous rock.

We conclude that of the two anomalous chips we have analysed, 10056 seems to be related to the "microgabbro" clan B-1 and thus does not pose any extraordinary problems of provenance or petrogenesis. Rock 10050, however, may well have originated as an impact-mobilized fragment from a geologic unit distinct from that immediately underlying the regolith at the Apollo 11 landing site. If so, a detailed study of this rock would be very valuable.

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elemental abundances in selected individual rocks (ppm)

10050	10018	10021	10056	10060	10061
—	1.4 ± 0.3 2.1 ^a	—	1.6 ± 0.3 2.2 ^q 2.6 ^p	2.1 ± 0.4 1.7 ^q	—
1990 ± 120 3900 ^f 2100 ⁱ	1590 ± 100 1660 ^a 1700 ^b 1050 ^a	1560 ± 90 1770 ⁱ 1700 ^f 1580 ^p	1970 ± 120 2000 ^q 2140 ^p	1650 ± 100 1600 ^q 1800 ⁱ 1620 ^a 1340 ⁿ	1450 ± 80 1820 ⁱ 1700 ^b 2400 ^f
13.6 ± 0.5 15.2 ^c 10 ^f	32.7 ± 0.8 32 ^a 35 ^b 24.0 ^a	30.7 ± 0.7 33 ^a 13 ^f	11.9 ± 0.4 15 ^q 14 ^p	31.6 ± 0.6 32 ^q ~30 ⁿ 30.0 ^a	33.7 ± 0.6 35 ^a 23 ^b 34.2 ^a 12 ^f
88.9 ± 1.0 170 ^f	60.3 ± 0.7 66 ^a 69 ^a	61.8 ± 0.8 72 ^a 68 ^f	91.6 ± 1.6 97 ^q 109 ^p	64.0 ± 0.7 70 ^q 70 ⁿ 70 ^a	59.6 ± 0.7 67 ^a 55 ^f
117 ± 9 80 ^f	67 ± 14 60 ^a 51 ^b	73 ± 9 60 ^a 22 ^f	47 ± 9 56 ^q	58 ± 8 62 ^q ~90 ⁿ	80 ± 6 60 ^a 34 ^b 32 ^f
2120 ± 60 4800 ^f 2400 ⁱ	1880 ± 60 2340 ^a 1950 ^b 1900 ^a	1950 ± 50 2480 ⁱ 2500 ^f	1950 ± 50 1400 ^q 1410 ^p	1880 ± 60 2200 ^q 2300 ⁱ 2800 ^a 1820 ^a	1930 ± 50 2730 ^a 1940 ^b 3000 ^f

j. PERKINS *et al.* (1970); gamma-ray spectrometry.

k. PHILPOTTS and SCHNEFZLER (1970); isotope dilution.

l. ROSI *et al.* (1970); X-ray fluorescence, wet chemical.

m. SILVER (1970); isotope dilution.

n. SMALES *et al.* (1970); diverse techniques.

o. TATSUMOTO and KOSHLI (1970); isotope dilution.

p. TUREKIAN and KHARKAR (1970); activation analysis.

q. WÄNKER *et al.* (1970); activation analysis.

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Instrumental activation techniques for the Analysis of meteorites and lunar materials

ALTHOUGH ACTIVATION ANALYSIS was first used over 30 years ago,¹ this technique only came into general use several years after the end of World War II. Since then, the applications have spread to many fields, as the recent comprehensive bibliography produced by the National Bureau of Standards well illustrates.² It is probably true that activation analysis, especially by neutrons, has had its greatest impact in meteorite studies, where the high sensitivities and comparative freedom from laboratory and reagent contamination have enabled radiochemical analyses to be made routinely at microgram to nanogram levels. Nondestructive neutron activation analyses have been made using NaI(Tl) gamma-ray scintillation spectrometry,³ but the poor energy resolution severely restricts the application of this technique. In favorable cases where the indicator radionuclide has two or more gamma rays in cascade, very specific determinations have been carried by NaI(Tl) coincidence counting⁴ and by single parameter⁵ and multi-parameter⁶ coincidence spectrometry. The advent of the high resolution, solid-state detectors has added a new dimension to activation analysis, as it makes possible the nondestructive determination of a large number of major, minor, and trace elements in materials of geochemical and cosmochemical interest (see, for example, Ref. 7). A somewhat different approach to the nondestructive analysis of meteorites and rocks has grown from the commercial availability of small 14-Mev neutron generators. The major application of these instruments has been the nondestructive analysis

of the lighter, more abundant elements.^{8,9}

The application of these techniques has been particularly valuable for the analysis of meteorites where specimens are often rare and the amounts available for analysis small. The experience gained by a number of laboratories in this type of analysis was turned to great advantage when the first lunar rocks were returned to earth. It is the purpose of this article to summarize the principles of non-destructive activation methods that can be applied to meteoritic and lunar material.

Principles and techniques

The activation method is based on induced nuclear reactions of naturally occurring isotopes which yield radioactive indicator nuclides. Regardless of the nature of the activating flux, the activity of the indicator radionuclide after activation can be given by

$$A = n f \sigma G D \quad (1)$$

where

- A = activity of product radionuclide, disintegrations sec⁻¹
- n = number of the target nuclide atoms in the sample
- f = bombarding particle flux, particles cm⁻² sec⁻¹
- σ = activation cross section, cm²
- G = growth, or saturation factor = $(1 - e^{-\lambda t})$
- D = decay factor = $(e^{-\lambda_d t_d})$
- λ = decay constant of the product radionuclide
- t = time
- t, t_d = irradiation and decay, respectively.

Equation (1) has two variables, G and D , which can be chosen to favor the analyses required. The growth factor G is generally chosen to be about 0.5; that is, the sample is irradiated for one half-life ($t_{1/2} = \lambda/\ln 2$) of the product nuclide.

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The decay factor D can be adjusted so that short-lived interfering radionuclides are allowed to decay before counting. Here again, one half-life is generally an acceptable period.

In most practical situations, the values for the flux, cross section, and absolute activity are difficult to evaluate precisely, and it is customary to irradiate a standard of known composition simultaneously with the unknown sample. After a suitable decay the standard and sample are sequentially counted with the same detector system so that

$$W_{\text{sam}} = W_{\text{std}} \times \frac{R_{\text{sam}}}{R_{\text{std}}} \times \frac{D_{\text{std}}}{D_{\text{sam}}} \quad (2)$$

where R is the experimental counting rate, W is the weight of the element, and the subscripts refer to sample and standard, respectively.

In some applications it is not convenient to irradiate sample and standard simultaneously. Samples and standards may be irradiated and counted sequentially, and the relative flux can be monitored independently. If the irradiation and counting times are the same, the elemental abun-

dance can then be derived by

$$W_{\text{sam}} = W_{\text{std}} \times \frac{M_{\text{std}}}{M_{\text{sam}}} \times \frac{R_{\text{sam}}}{R_{\text{std}}} \times \frac{D_{\text{std}}}{D_{\text{sam}}} \quad (3)$$

where M is the integrated monitor count.

14-Mev neutron activation analysis

A convenient laboratory source of fast neutrons is provided by a simple Cockcroft-Walton generator. Deuterium is doubly ionized in an ion source and accelerated by a series of electrodes to an energy of about 150 kev. Neutrons are produced by the reaction



The yield is very nearly isotropic, and the energy of the neutrons is approximately 14 Mev at the target position. Many applications of 14-Mev neutron activation utilize short-lived indicator radionuclides, and therefore time is of the essence when the irradiated sample is transferred to the counting position. Pneumatic sample transfer systems are almost universally employed, and these can be cheaply made from low density polyethylene tubing.¹⁰ Encapsulated samples may be propelled by compressed nitrogen or vacuum,^{11, 12} and irradiation, delay, and counting times are generally controlled by preset electronic timing circuits.

Meteorite and terrestrial rock specimens are usually powdered before analysis, so that a representative sample may be obtained, but for lunar rocks the small pieces provided must often be kept intact. The samples should be prepared and encapsulated under dry nitrogen if oxygen determinations are required. In our laboratory, samples are sealed in polyethylene vials using heat-shrinkable tubing to effect a neat gastight closure.¹⁰ These are reproducibly located in 2-dram, polyethylene, snap-top pill packs that are heat-sealed with a beveled iron to give a truncated conical shape to the completed "rabbit."

The precision and accuracy of the 14-Mev method are influenced by a number of factors that have been reviewed recently.¹⁴

In the determination of major elements in terrestrial rock samples, good precision has been obtained by irradiating sample and standard simultaneously^{15, 16} using a dual-transfer, biaxial-rotator system. For reasons connected with the statistical advantages of comparing each sample with several standards, in our laboratory the samples and standards are irradiated sequentially using a single-transfer system shown schematically in Figure 1. By detailed attention to beam stability

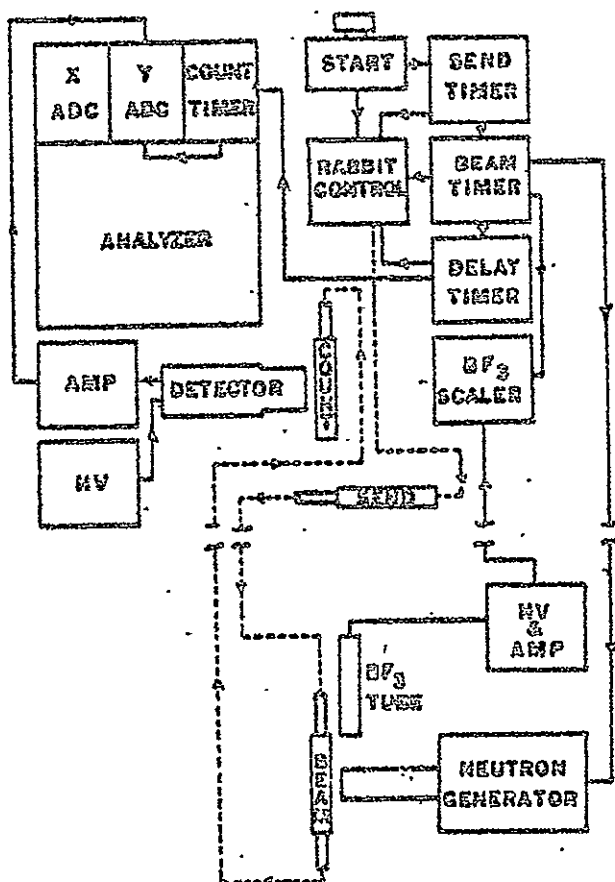


Figure 1 Block diagram of single-transfer 14-Mev neutron activation system.

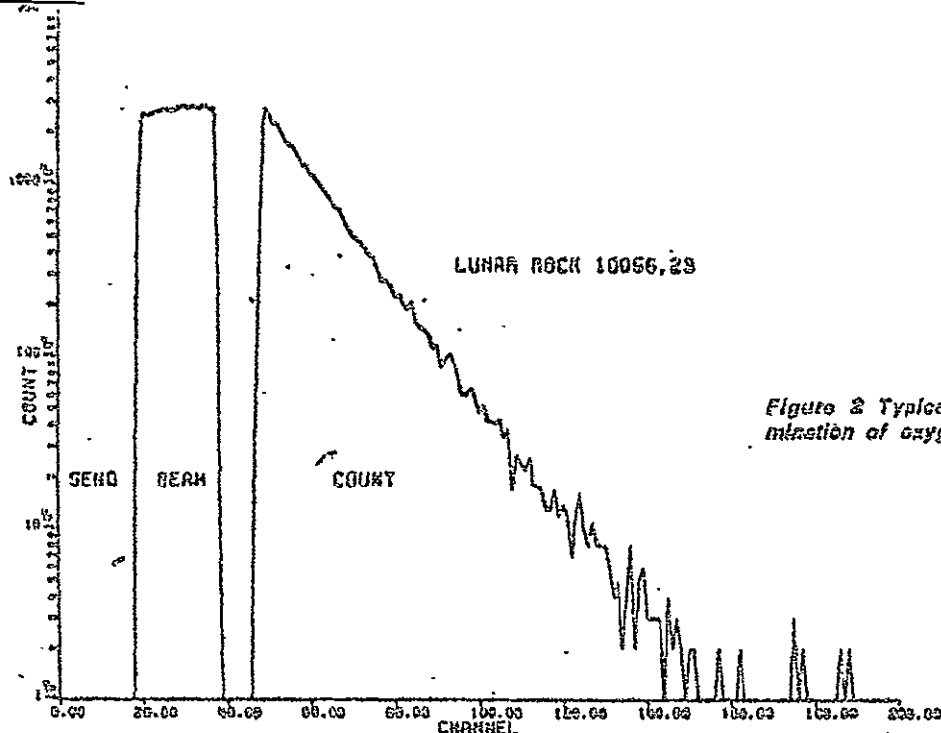


Figure 2 Typical multiscale pass for the precise determination of oxygen in meteorites and lunar rocks.

NOT REPRODUCIBLE

and flux uniformity and by careful quality control of the neutron monitoring system, it is possible to approach the precision attainable by biaxial rotation.¹⁷

The major products of 14-Mev neutron reactions on each element have been compiled,¹⁸ and a study of the analytical interferences has been made.¹⁹ Interferences may be of two types. Type I are primary interferences where the indicator radionuclide sought is produced by another reaction on a different element. Type II are spectral interferences in which a radionuclide is produced which has a photon energy unresolvable from that of the indicator radionuclide by the chosen detection

method [usually NaI(Tl) spectrometry]. Reactions that are of interest in the analysis of meteorites and lunar rocks are summarized in Table I. It will be noted that cross sections are given in millibarns, where 1 barn = 10^{-24} cm². The high energy ¹⁶N gamma rays are very specific,²⁰ and this has enabled the development of a multiscale method for oxygen, which circumvents many problems associated with timing errors and variations in neutron flux.¹⁷ In this method both the output of the neutron monitor and the ¹⁶N activity are recorded on the same multiscale pass. This is illustrated by Figure 2. By suitable computer processing it is possible to compensate accurately for flux and

Table I

Elements of cosmochemical interest which may be determined by 14-Mev neutron activation

Element	Analytical reaction	Product gamma energy, Mev	Product half-life	Type I Interference	Type II Interference	Interference gamma energy, Mev	Interference half-life
O	¹⁶ O(n,p) ¹⁶ N	6.13 7.12	7.35 sec	¹⁹ F(n,α) ¹⁶ N	¹¹ B(n,p) ¹¹ Be	6.8 8.0	13.6 sec
Mg	²⁴ Mg(n,p) ²⁴ Na	1.37 2.75	15 hr	²⁷ Al(n,α) ²⁴ Na	⁴¹ K(n,p) ⁴¹ Ar	1.20	1.83 hr
Al	²⁷ Al(n,p) ²⁷ Mg	0.84 1.01	9.6 min	³⁰ Si(n,α) ²⁷ Mg	⁵⁶ Fe(n,p) ⁵⁶ Mn β ⁺ annihilation	0.65 1.02	2.68 hr
Si	²⁸ Si(n,p) ²⁸ Al	1.78	2.3 min	²⁷ Al(n,γ) ²⁶ Al ³¹ P(n,α) ²⁸ Al	⁵⁶ Fe(n,p) ⁵⁶ Mn ⁴⁸ Ti(n,p) ⁴⁸ Sc	1.31 1.76	2.68 hr 57.5 min
Ti	⁴⁸ Ti(n,p) ⁴⁸ Sc	0.14	20 sec	⁴⁸ Sc(n,γ) ⁴⁸ Sc	⁵⁷ Fe(n,p) ⁵⁷ Mn [†]	1.37	1.7 min
Fe	⁵⁶ Fe(n,p) ⁵⁶ Mn	0.85 1.81	2.68 hr	⁵⁶ Mn(n,γ) ⁵⁶ Mn ⁵⁹ Co(n,α) ⁵⁶ Mn	⁴⁸ Ti(n,p) ⁴⁸ Sc	1.76	57.5 min

timing variations.

About 1 min after irradiation, ^{26}Al produced from Si is the major gamma activity visible in a silicate rock, and interferences are generally very small.²¹ A major problem in the precise determination of silicon has been associated with the analyzer dead time. This can be minimized by controlling the analyzer with an external timer set for an elapsed time E . The actual live time L is stored in the analyzer. The empirical integrated gamma activity I is then corrected by a factor E/L to give a more representative integrated count. In some cases a more precise mathematical treatment may be needed.

A recent innovation in analyzer design which claims a "zero dead time" will be of considerable value for the measurement of short-lived activities. This system stores counts arriving during a dead-time period, and then transfers them to the same address as the next count to arrive after the analyzer is again enabled. Since the dead-time correction is important only for high count rates, it can be seen that the numbers of counts involved make this sampling procedure statistically sound.

The integration of the photopeak in the gamma spectrum is carried out in our laboratory using the procedure outlined by Sterlinski.²² This is a relatively simple mathematical method for obtaining good statistical data, which requires no assump-

tions to be made about peak shape or instrumental resolution. It enables the spectrum shape of the sample and standard to be compared and can detect nonlinearities in the baseline under the peak being integrated.

The analyses of the lunar samples for aluminum were based upon the 0.84-Mev gamma ray of ^{27}Mg . The interference from silicon is a large one, and it was found empirically that 1% silicon is equivalent to 0.03% aluminum. In order to minimize the effects of any residual error in this correction, standards were chosen whose aluminum-to-silicon ratio bracketed those of the lunar rocks.

In the Apollo 11 rocks the iron abundance is high and constitutes a serious interference to the aluminum determination. This was empirically corrected for by recounting the sample after approximately 2 hr. By this time ^{27}Mg had largely decayed, and the interfering ^{56}Mn photopeak could be precisely evaluated. From the same spectra it was also possible to derive iron abundances. Magnesium and titanium analyses by 14-Mev neutron activation have not yet been made on lunar rocks, though in principle these measurements are feasible.

NaI(Tl) coincidence spectrometry

The energy discrimination of NaI(Tl) detectors is often inadequate for the resolution of the com-

Table 2
Elements of cosmochemical interest which may be determined by gamma-gamma coincidence

Element	Reaction	Major coincidence, Mev	Half-life	Element	Reaction	Major coincidence, Mev	Half-life
Sodium	$^{23}\text{Na}(n,\gamma)^{24}\text{Na}$	1.37-2.75	15 hr	Barium	$^{130}\text{Ba}(n,\gamma)^{131}\text{Ba}$	0.12-0.50	12 days
Scandium	$^{45}\text{Sc}(n,\gamma)^{46}\text{Sc}$	0.89-1.12	84 days	Lanthanum	$^{139}\text{La}(n,\gamma)^{140}\text{La}$	0.49-1.60	40 hr
Manganese	$^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$	0.84-1.81	2.6 hr	Samarium	$^{152}\text{Sm}(n,\gamma)^{153}\text{Sm}$	0.07-0.10	47 hr
Cobalt	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	1.17-1.33	5.2 yr	Europium	$^{151}\text{Eu}(n,\gamma)^{152}\text{Eu}$	0.122-0.96	12 yr
Nickel	$^{58}\text{Ni}(n,p)^{58}\text{Co}$	0.51 (β^+) -0.81-1.54	71 days	Hafnium	$^{180}\text{Hf}(n,\gamma)^{181}\text{Hf}$	0.13-0.48	42.6 days
Copper	$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$	0.51-0.51 (β^+)	13 hr	Tantalum	$^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$	0.22-1.23	115 days
Zinc	$^{64}\text{Zn}(n,\gamma)^{65}\text{Zn}$	0.51-0.51 (β^+) -1.12	245 days	Tungsten	$^{186}\text{W}(n,\gamma)^{187}\text{W}$	0.13-0.55	24 hr
Selenium	$^{74}\text{Se}(n,\gamma)^{75}\text{Se}$	0.14-0.26	120 days	Iridium	$^{191}\text{Ir}(n,\gamma)^{192}\text{Ir}$	0.32-0.47	74.2 day
Bromine	$^{81}\text{Br}(n,\gamma)^{82}\text{Br}$	0.65-0.78	36 hr	Thorium	$^{232}\text{Th}(n,\gamma)^{233}\text{Th}$ β ^{233}Pa	U x-ray-0.31	27.0 day
Tin	$^{118}\text{Sn}(n,\gamma)^{119}\text{mSn}$	0.16-0.16	14 days	Uranium	$^{238}\text{U}(n,\gamma)^{239}\text{U}$ β ^{239}Np	0.07-0.21	2.35 day
Cesium	$^{133}\text{Cs}(n,\gamma)^{134}\text{Cs}$	0.61-0.80	2.1 yr				

plex gamma spectra of an irradiated rock or meteorite. The specificity may be improved if the indicator radionuclide has two or more gamma rays which are in cascade, that is, which are emitted to all practical purposes simultaneously. Except in very specialized cases, the neutron output of 14-Mev generators is not high enough for use with the lower detector efficiency associated with coincidence detection. Most activation analyses by the coincidence method require the high thermal neutron flux available in a nuclear reactor. A compilation of elements that may be determined by gamma-gamma coincidence has been made by Wing and Wahlgren,²⁵ who also calculated sensitivities for thermal neutron irradiation. A selection of elements whose determination by coincidence may have some application to meteorite and lunar research is listed in Table 2. The application of the coincidence technique is readily illustrated by

the simple example of the determination of cobalt in iron by activation analysis.²⁴ Thermal neutron irradiation of cobalt induces the reaction $^{59}\text{Co}(n, \gamma)^{60}\text{Co}$. Iron under the same conditions undergoes the reaction $^{56}\text{Fe}(n, \gamma)^{56}\text{Fe}$. The major gamma rays of ^{60}Fe have energies of 1.10 and 1.29 Mev, which obscure the small ^{60}Co peaks at 1.17 and 1.33 Mev. However, the cobalt peaks are in coincidence, and by using two NaI(Tl) detectors and appropriate coincidence mixing circuitry it is possible to determine the cobalt content of iron nondestructively.

More recently a similar approach has been applied to the nondestructive determination of iridium in chondritic meteorites.²⁶ A block diagram of the single parameter coincidence spectrometry is shown in Figure 3. By use of this method it has been possible to determine iridium nondestructively at levels between 10^{-8} and 10^{-7} g g⁻¹ using only a few tenths of a gram of sample.

The single parameter spectrometer has some grave limitations. It is often difficult to discriminate between true photopeak coincidences and Compton-Compton coincidences, and the spectrometer needs to be carefully adjusted for each radionuclide sought. In addition, only half of the coincidence pulses recorded are generally registered in the spectrum. This deficiency does not occur with 0.51-0.51 annihilation coincidences, but unfortunately in many cases these coincidences are far from specific. Iridium is another favorable case, where several coincident gamma rays occur close to 0.3 Mev.

In the coincidence system just described, selectivity is attained by the careful adjustment of the single-channel analyzer windows. This has the big disadvantage that generally only one radionuclide can be determined at a time. To avoid these problems, a multiparameter gamma-gamma coincidence spectrometer can be used.²⁶ A block diagram of a simple multiparameter system is shown in Figure 4. The 2.5-cm-thick lead shield between the two 7.5- x 7.5-cm NaI(Tl) detectors serves to reduce coincidences due to backscattering. A typical spectrum of the long-lived activity in a lunar rock is shown in Figure 5. The energy range covered is roughly 0.1 to 1.5 Mev.

Quantitative determinations can be carried out by visual spectrum stripping or by suitable computer processing. Visual stripping can be carried out quite precisely, and the mean relative deviation of triplicate stripping generally averages 1 to 2%.

There have been few applications of gamma-gamma coincidence techniques to the analysis of

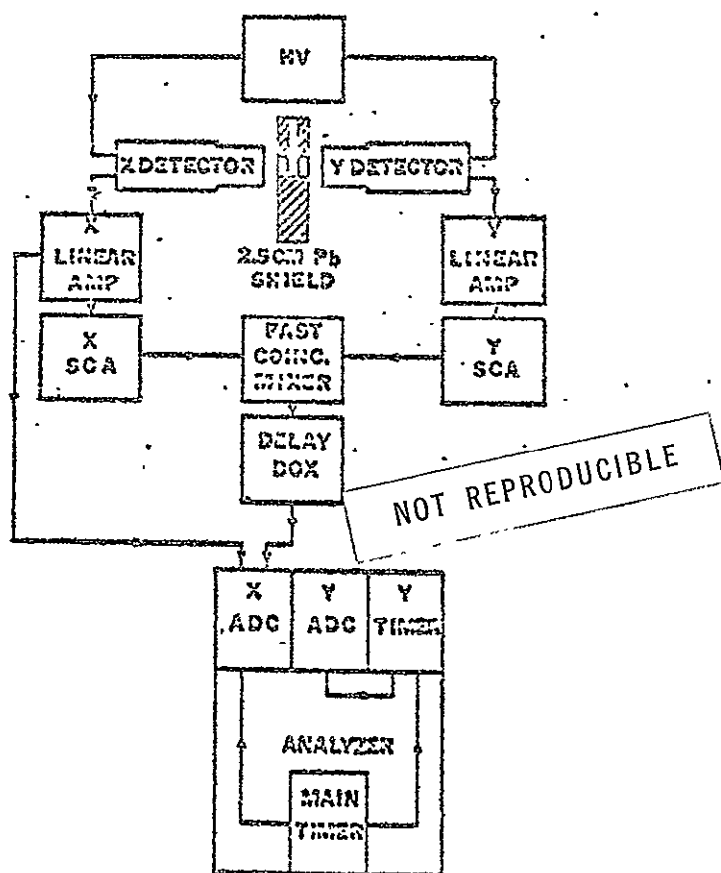


Figure 3 Block diagram of a single-parameter coincidence spectrometer used to determine iridium in meteorites.

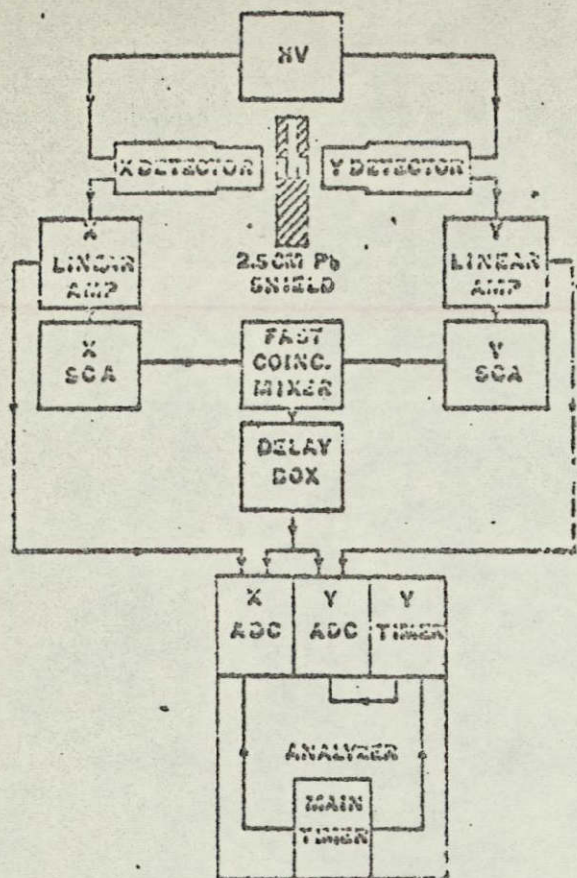


Figure 4 Block diagram of a multiparameter coincidence spectrometer used for neutron activation analysis of meteorites and lunar rocks.

meteorites and lunar rocks. An early application of the coincidence method used the 0.51-0.51-Mev annihilation coincidence of ^{64}Cu to determine copper in meteorites.³⁷ The abundance of bromine has been measured in stony meteorites using the cascade gamma rays of ^{82}Br (Ref. 28). The elements sodium, scandium, cobalt, nickel, and iridium have also been determined in chondritic meteorites by single and multiparameter coincidence spectrometry.^{3,6} The latter technique is currently being applied at the University of Kentucky to the determination of a number of elements in Apollo 11 rocks and soils.

High resolution Ge(Li) spectrometry

The coincidence methods previously outlined have the obvious limitation that they can only be applied to radionuclides with abundant coincident gamma rays. The resolution of NaI(Tl) detectors is not good enough to identify and determine unequivocally any but the most abundant photopeaks. However, the recent advent of lithium-drifted germanium detectors has made direct nondestructive multielement activation analysis a very viable proposition. A good solid-state Ge(Li) detector, with stable noise-free electronics, can yield resolution for the ^{137}Cs peak of 2- to 4-keV full width at half maximum, as opposed to a value of about 50 keV using a good NaI(Tl) crystal. Naturally enough, the high resolution is accompanied by some less desirable features. Because of the lower atomic number, the photopeak efficiency for a 1-Mev gamma ray using a large (35- to 40-cm³) Ge(Li) detector is only about 5% of that for a standard 7.5- x 7.5-cm NaI(Tl) detector, and the comparison is even less favorable at higher energies. In addition, the Ge(Li) detector must be kept at liquid nitrogen temperatures at all times, and very low noise amplifiers are essential to obtain the best resolution of which the detector is capable. The result is that a Ge(Li) system based on a 35- to 40-cm³ active volume detector can be 2 to 3 times more expensive than a 7.5- x 7.5-cm NaI(Tl) spectrometry assembly.

The application of Ge(Li) spectrometry to non-destructive reactor activation analysis of material of geochemical and cosmochemical interest has become widespread since the now classic work on U. S. Geological Survey standard rocks by Gordon et al.³⁸

Elements that may be determined in rocks and meteorites by high resolution gamma-ray spectrometry following reactor neutron activation are summarized in Table 3.

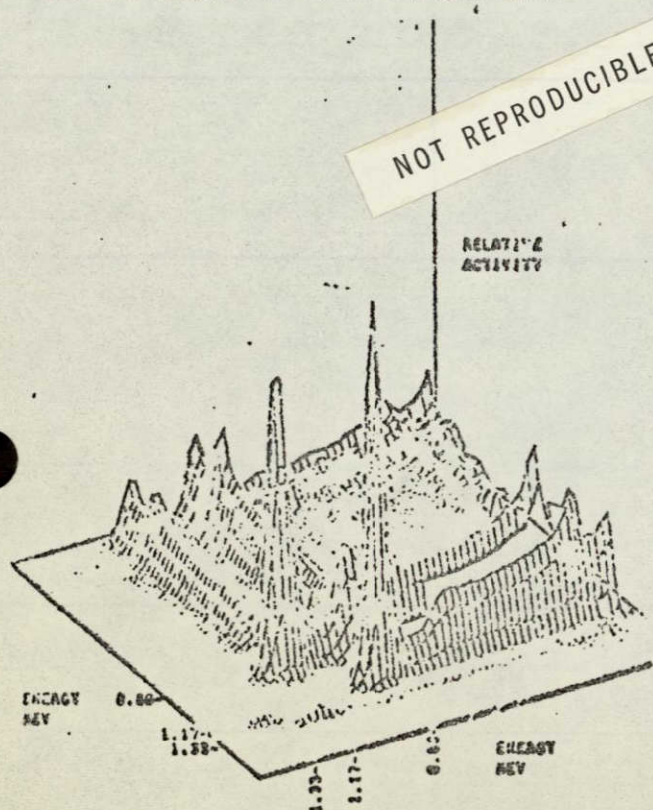


Figure 5 Typical multiparameter coincidence spectrum of the long-lived gamma-ray activity in a neutron-irradiated lunar rock. The two large peaks are due to 0.69-Mev-1.12-Mev coincidences of ^{46}Sc . Smaller peaks are due to 1.17-Mev-1.33-Mev ^{60}Co coincidences and to 0.13-Mev-0.43-Mev coincidences of ^{140}La .

Photoactivation

Irradiation by high energy bremsstrahlung photons can induce analytically useful reactions of the types (γ, γ') , (γ, n) , and (γ, p) . Although photoactivation techniques can be applied successfully to the determination of small traces of light elements, they are also useful for the determination of major and minor components in meteorites and lunar materials. In particular, photoactivation has been applied to the determination of elements such as magnesium, calcium, and titanium,²⁹ which are not easily determined by neutron activation techniques. Limited access to high intensity sources of energetic photons has restricted the widespread use of this method.

Delayed neutron emission

When certain heavy elements are irradiated with neutrons or other particles, fission takes place. Probably the best-known example is the fission of ²³⁵U induced by thermalized neutrons. The fission fragments formed lie on the extreme neutron-rich side of the stability line, and they decay by neutron emission as well as by the more usual mechanism of beta decay. Techniques have been developed³⁰ in which samples are irradiated for a few seconds, then quickly transferred to a continuing assembly of boron trifluoride neutron detectors in which they are counted for 30 sec. This method is quite specific for fissionable material. If the irradiating neutron energy is below the ²³²Th fission threshold,

Table 3

Elements of cosmochemical interest which may be determined nondestructively by high resolution Ge(Li) spectrometry

Element	Reaction	Analytical gamma ray, Kev	Half-life	Element	Reaction	Analytical gamma ray, Kev	Half-life
Sodium	²³ Na(<i>n,γ</i>) ²⁴ Na	1369	15 hr	Cerium	¹⁴⁰ Ce(<i>n,γ</i>) ¹⁴¹ Ce	145	33 day
Potassium	⁴¹ K(<i>n,γ</i>) ⁴² K	1524	12 hr	Neodymium	¹⁴⁶ Nd(<i>n,γ</i>) ¹⁴⁷ Nd	91, 531	11 day
Scandium	⁴⁸ Sc(<i>n,γ</i>) ⁴⁸ Sc	889, 1120	84 day	Samarium	¹⁵² Sm(<i>n,γ</i>) ¹⁵³ Sm	103	47 hr
Chromium	⁵⁰ Cr(<i>n,γ</i>) ⁵¹ Cr	320	28 day	Europium	¹⁵¹ Eu(<i>n,γ</i>) ¹⁵² Eu	122, 245, 779, 1408	12 yr
Manganese	⁵⁵ Mn(<i>n,γ</i>) ⁵⁶ Mn	847, 1811	2.6 hr		¹⁵³ Eu(<i>n,γ</i>) ¹⁵⁴ Eu	724, 1277	16 yr
Iron	⁵⁸ Fe(<i>n,γ</i>) ⁵⁹ Fe	1100, 1291	45 day	Gadolinium	¹⁵² Gd(<i>n,γ</i>) ¹⁵³ Gd	97, 103	242 day
Cobalt	⁵⁹ Co(<i>n,γ</i>) ⁶⁰ Co	1173, 1332	5.3 yr	Terbium	¹⁵⁹ Tb(<i>n,γ</i>) ¹⁶⁰ Tb	299, 963, 966	72 day
Rubidium	⁸⁵ Rb(<i>n,γ</i>) ⁸⁶ Rb	1077	19 day	Dysprosium	¹⁶⁴ Dy(<i>n,γ</i>) ¹⁶⁵ Dy	95	2.3 hr
Zirconium	⁹⁴ Zr(<i>n,γ</i>) ⁹⁵ Zr	725, 757	65 day	Thulium	¹⁶⁹ Tm(<i>n,γ</i>) ¹⁷⁰ Tm	84	130 day
	↓β			Ytterbium	¹⁶⁸ Yb(<i>n,γ</i>) ¹⁶⁹ Yb	63, 177, 198	32 day
	⁹⁵ Nb	768	35 day		¹⁷⁴ Yb(<i>n,γ</i>) ¹⁷⁵ Yb	283, 395	4.2 day
Antimony	¹²¹ Sb(<i>n,γ</i>) ¹²² Sb	566	2.8 day	Lutetium	¹⁷⁶ Lu(<i>n,γ</i>) ¹⁷⁷ Lu	208	6.7 day
	¹²³ Sb(<i>n,γ</i>) ¹²⁴ Sb	1691	60 day	Hafnium	¹⁸⁰ Hf(<i>n,γ</i>) ¹⁸¹ Hf	133, 482	43 day
Cesium	¹³³ Cs(<i>n,γ</i>) ¹³⁴ Cs	605, 796	2.1 yr	Tantalum	¹⁸² Ta(<i>n,γ</i>) ¹⁸³ Ta	68, 100, 1122	115 day
Barium	¹³⁰ Ba(<i>n,γ</i>) ¹³¹ Ba	216, 373, 496	12 day	Thorium	²³² Th(<i>n,γ</i>) ²³³ Th	94, 98, 312	
Lanthanum	¹³⁹ La(<i>n,γ</i>) ¹⁴⁰ La	329, 487, 816, 1596	40 hr		↓β	416	27 day
					²³³ Pa		

it is a sensitive means of determining uranium in natural materials. By enclosing samples in cadmium to absorb thermal neutrons, thorium can be determined using the same general technique by exposure to a fast neutron flux.

Other techniques, such as prompt gamma-ray counting and charged-particle activation, have yet to be applied, to any extent, to the analysis of meteorites and lunar rocks. Charged-particle activation is particularly suited to the analysis of trace elements in surfaces, and could well find important applications in the study of solar wind implantation on the surface of lunar rocks.

Conclusion

The preceding discussion has indicated the scope of activation techniques as applied to the non-destructive elemental analysis of small, rare samples such as lunar rocks and meteorites. The advantages of high sensitivity, accuracy, freedom from reagent and laboratory contamination, and speed, coupled with the potential of nondestructive analyses for many elements, suggest that this technique should be a part of any modern analytical facility. For 14-Mev neutron activation a modest but adequate sealed-tube neutron generator and the necessary counting instrumentation may be obtained for under \$25,000. This price is not out of line with the investment made for other modern analytical instruments.

For trace element determinations via reactor neutron irradiation, on-site irradiation facilities are not always required. Many university and commercial nuclear reactor facilities offer irradiation services at modest prices.²¹ For this type of work the only investment required in addition to the basic counting instrumentation is for an adequate shielded shipping container. The absence of a nuclear reactor at the University of Kentucky has not been a serious handicap, as evidenced by the many thousands of trace element determinations made by this group. Shipping delays generally limit the selection of indicator radionuclides to those having half-lives of at least 10 hr.

The widespread use of activation techniques in the NASA program for the analysis of the returned lunar samples is a concrete example of the utility of the method under conditions where accurate, nondestructive data on large numbers of samples were required in a minimal time.

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SECTION VIII

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PRECISE DETERMINATION OF OXYGEN AND SILICON IN CHONDRITIC METEORITES BY 14-MeV NEUTRON ACTIVATION WITH A SINGLE TRANSFER SYSTEM

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The significance of the chondritic meteorites to the study of solar system elemental abundances has recently been reviewed¹. The chondrites fall into well defined chemical and petrological classes, with characteristic oxygen and silicon abundances². Every meteorite fall is unique, and museum curators are reluctant to distribute large samples. There is a considerable advantage, therefore, in the use of non-destructive techniques, and especially those that require only small amounts of material.

The non-destructive analysis of meteorites for silicon and oxygen by 14-MeV neutron activation is rapid and accurate^{2,3}. In these single transfer methods, samples and comparator standards were irradiated separately and counted sequentially, and corrections made for variations in neutron flux by means of the output of a neutron monitor. More recently, assemblies have become available which allow the irradiation of the sample and comparator standard simultaneously. Uniform exposure to the neutron beam is achieved by biaxial rotation. Oxygen and silicon have been analysed in a suite of standard USGS rocks with a biaxially rotating target assembly and a dual transfer system^{4,5}. Results on 2.5–3 g splits of well mixed rock powders were reproducible to $\pm 0.25\%$ oxygen and $\pm 0.12\%$ silicon (mean standard deviation). In this application sample and standard were counted simultaneously on separate detectors. Differences in the geometry of the two irradiation positions and the efficiency of the two detectors were compensated by a four-cycle irradiation sequence. Each irradiation position and detector combination was used for both sample and standard, and the resulting counts were pooled for the abundance calculations. Stable beam conditions are essential for the compensation to be valid. Reproducibility for a single determination cannot be estimated, as each individual value is the mean of four irradiation-counting cycles.

A dual transfer-biaxial rotator system for the 14-MeV neutron activation of oxygen has been reported which avoids the problems associated with the dual detector system⁶. Sample and standard were irradiated simultaneously, but were counted sequentially. The γ -ray energy region between 4.8 and 8.0 MeV was registered by a multiscaler, so that precise timing of the sample and standard counting sequence was achieved. The precision of the ratio of activities of two pure benzoic standards agreed with that expected hypothetically from the counting statistics. The sequential counting system gives considerably poorer counting statistics than a single irradiation-transfer system under identical conditions, and the simpler irradiation assembly of

the single system allows the sample to be more favorably positioned in the neutron beam.

The disadvantages of the dual transfer-biaxial rotator system for large samples are greatly outweighed by the precision achieved under optimum conditions. For meteorites, the available sample is generally small and the loss in precision from poorer counting statistics is more serious. There are definite advantages, therefore, in the use of the single transfer system, though improvement in precision is needed.

An evaluation of sources of random error was made. In the analysis for oxygen precise timing was important, and errors could arise from fluctuations in beam intensity if the integrated neutron dose only was recorded. These considerations were met by adapting the multiscaler approach to the single transfer system. The output of the boron trifluoride neutron monitor and the induced activity were recorded on the same multiscaler pass. By mathematically treating each channel recording the relative neutron flux as an individual irradiation, changes in beam intensity could be precisely compensated.

Requirements for precise silicon analyses were rather different. Improvements were made to the statistical treatment of the γ -ray photopeak evaluation and refinements were introduced to the method of analyser live-time correction as applied to short-lived radionuclides.

NUCLEAR DATA

Analyses were made by means of 14.7-MeV neutrons produced by the reaction $^3\text{H}(\text{d},\text{n})^4\text{He}$.

Irradiation of oxygen and silicon with these essentially monoenergetic fast neutrons induces several reactions which are summarized in Table I. The most sensitive reaction for oxygen is that leading to the production of 7.35-sec ^{16}N , whose energetic γ -rays are highly specific for this radionuclide. The most convenient indicator nuclide for silicon is 2.3-min ^{28}Al , produced by an (n,p) reaction on the abundant ^{28}Si isotope. The 1.78-MeV γ -ray of ^{28}Al is not as unequivocal as the high-energy ^{16}N photons, but for several minutes after a short 14-MeV neutron

TABLE I
14-MeV NEUTRON REACTIONS ON OXYGEN AND SILICON

Element	Reaction	Isotope abundance (%)	Cross section (mb)	Half life	Gamma energy (MeV)	Branching ratio (%)
Oxygen	$^{16}\text{O}(\text{n},\text{p})^{16}\text{N}$	99.8	33	7.35 sec.	6.13	68
					7.12	5
	$^{16}\text{O}(\text{n},2\text{n})^{15}\text{O}$		0.5	2 min	0.511	100
	$^{17}\text{O}(\text{n},\text{p})^{17}\text{N}$	0.037	112	4.1 sec	—	—
Silicon	$^{18}\text{O}(\text{n},\alpha)^{15}\text{C}$	0.20	11	2.3 sec	5.3	—
	$^{28}\text{Si}(\text{n},\text{p})^{28}\text{Al}$	92.2	250	2.3 min	1.78	100
	$^{29}\text{Si}(\text{n},\text{p})^{29}\text{Al}$	4.7	100	6.6 min	1.28	94
					2.43	6
	$^{30}\text{Si}(\text{n},\alpha)^{27}\text{Mg}$	3.1	45-185	9.5 min	0.84	69
					1.07	30.4
					0.18	0.6

irradiation, it is the most prominent photopeak in the spectrum of a silicate rock or stony meteorite.

Sources of interference in 14-MeV neutron activation analysis have been discussed by MATHUR AND OLDHAM⁷, who classified interferences into two types. Type I are reaction interferences, where the indicator radionuclide is produced from elements other than that sought. Instrumental, or Type II, interferences arise from activities whose γ -rays are unresolvable by NaI(Tl) scintillation spectrometry. Possible interferences in the determination of oxygen and silicon are outlined in Table II.

TABLE II

INTERFERENCE REACTIONS IN THE DETERMINATION OF OXYGEN AND SILICON

	Reaction	Isotope abundance (%)	Cross section (mb)	Half life	Gamma energy (MeV)	Branching ratio (%)
Oxygen						
Type I interference	$^{19}\text{F}(\text{n},\alpha)^{16}\text{N}$	100	23			
Type II interference	$^{11}\text{B}(\text{n},\text{p})^{11}\text{Be}$	80	3	13.6 sec	6.81 7.99	4 2
Silicon						
Type I interference	$^{27}\text{Al}(\text{n},\gamma)^{28}\text{Al}$	100	0.5			
Type II interference	$^{31}\text{P}(\text{n},\alpha)^{28}\text{Al}$	100	140			
Type II interference	$^{56}\text{Fe}(\text{n},\text{p})^{56}\text{Mn}$	91.7	115	2.58 h	1.81	29

The interference of fluorine can be serious, as this element produces ^{16}N activity equivalent to about 0.6 of its weight of oxygen. An empirical determination of this interference⁴ shows that 0.1% fluorine is equivalent to 0.0415% oxygen. The low (n,p) cross section for ^{11}B and the low branching ratio of the high-energy γ -rays of ^{11}Be mitigate against interference from this element, and boron-to-oxygen ratios up to 100 can be tolerated².

Interference to the silicon determination from the (n, γ) reaction on aluminum is insignificant for 14-MeV neutrons. There is some moderation of neutrons from shielding and empirical determinations of this interference⁸ indicate that 5% aluminum is equivalent to 0.01% silicon. Phosphorus in the specimen can interfere and 1% phosphorus pentoxide gives an activity equivalent to 0.21% silicon⁵. The Type II interference from iron can be neglected for rocks low in this element, but for chondrites a small correction must be applied. Calculations show that 1% iron is equivalent to 0.0033% silicon.

EXPERIMENTAL

Apparatus

Deuterons were accelerated by a Cockcroft-Walton generator (Kaman Nuclear, Colorado Springs, Model A-1250). Titanium targets containing 5-Ci ^3H were used for the production of 14-MeV neutrons. To ensure stable conditions, the combined

atomic and molecular deuterium beam was limited to 300–600 μA , and the accelerating potential to 140 keV. The beam was defocussed for more uniform target depletion and to improve the correlation between the sample neutron dose and the count recorded by the monitor⁹.

At the time of these analyses, the target had been bombarded for 100–150 mA min⁻¹, and was rather depleted. The neutron yield was about one third of that obtained from a new target and the sensitivities are typical rather than optimal.

The relative neutron flux was determined by means of a low-geometry boron (40% ¹⁰B) trifluoride tube. The stability of the neutron monitor has a marked effect on precision, and χ^2 -tests were carried out on the BF₃ detector system with a Pu–Be source before each series of determinations. The high voltage plateau, bias voltage and time constant curves were checked periodically. After amplification and pulse shaping the output of the neutron monitor was remotely recorded on a 6-decade scaler. For multiscaling applications, the neutron monitor was connected to a single-channel analyser, which provided suitable output pulses of uniform amplitude.

The details of the pneumatic sample transfer system and sequential programming circuit have been previously described¹⁰. Irradiated samples were counted in a 4 × 4" well-type NaI(Tl) detector, and the output was amplified by a double-delay line amplifier. Spectra were recorded on a Nuclear Data ND 2201 4096-channel analyser. For multiscaling, a pulse train of uniform height was obtained using the scaler output of a single-channel analyser.

Preparation of samples

Powders were prepared from four different interior portions of the Allende, Mexico, chondrite^{11,12}. Aliquots of 0.4–0.5 g were heat-sealed¹³ in 11/64-in internal diameter polyethylene vials. These were reproducibly located within 2 dram polyethylene snap top "pill packs" which were also heat-sealed ("rabbits").

The details of the source of the Allende specimens, and the weights of powder packed into each rabbit are summarized in Table III.

TABLE III
SAMPLING DETAILS OF ALLENDE SPECIMENS

Specimen number	Specimen weight (g)	Rabbit number	Sample weight (g)
S-5211a ^a	5.68	1845	0.4511
		1846	0.5113
		1847	0.4755
S-5211b ^a	6.20	1848	0.4710
S-5207a ^{b,c}	4.06	1849	0.4234
S-5207b ^{b,c}	3.17	1850	0.4694

^a Donated by C. B. MOORE.

^b Donated by R. S. CLARKE, JR.

^c U.S. National Museum specimen number USNM 3510.

Preparation of standards

Oxygen standards were prepared from primary standard-grade potassium dichromate (Mallinckrodt Chemical Works) which was dried to constant weight at 110°. The loss in weight was 0.04%.

Silicon standards were initially prepared from Specpure silica (Johnson-Matthey), ignited¹⁴ to constant weight at 600°. The weight loss was 1.71%. These standards were not entirely satisfactory and a primary standard was prepared from a piece of pure optical lens quartz, designated L-1. Comparator standards were packaged for irradiation in the same way as the samples.

Both oxygen and silicon standards were normalized to the pure quartz reference. The stoichiometry for the potassium dichromate agreed with the L-1 standard to within 0.4 rel. %, but the silicon abundance in Specpure silica was low by 1.9 rel. %. A determination of the oxygen in Specpure silica, normalized to L-1 quartz, yielded a result which was 2.3 rel. % higher than the stoichiometric value. Specpure silica is very finely divided and of large surface area; polymerized water may be present and may not be entirely removed even at 600°. The oxygen and silicon analyses of Specpure silica give a total of 100.39%, indicating good internal consistency for the inter-comparison of the three standards.

Determination of oxygen

At the beginning of each irradiation cycle, the amplified output of the boron trifluoride neutron monitor was connected through a single-channel analyser to the multiscaler input of the ND 2201 analyser. The dwell time of the multiscaler was set at 0.4 sec. The multiscaler pass was initiated and the irradiation cycle begun. The rabbit was irradiated for 15 sec during which time it was spun about its axis by a dry nitrogen jet. At the end of the irradiation, the rabbit was transferred back to the counting station. During the interval taken for the return of the sample, the multiscaler input was switched to the output of the detector assembly. A single-channel analyser integrated the energy region between 4.5 and 8.0 MeV.

The multiscaler pass continued for 90 sec after irradiation, to follow the decay to zero. The contents of the analyser memory were read out on to punched tape. The tapes were batch-processed on an IBM tape-to-card converter and the analytical data reduced by a computer.

In each series of analyses three samples and three potassium dichromate standards were irradiated in the sequence—standard, sample, sample, standard; the order was arranged so that a particular sample was not always irradiated between the same two standards.

Determination of silicon

The amplified output of the detector assembly was connected directly to an analogue-to-digital converter of the ND 2201 analyser. The discriminators and zero level were adjusted to analyse only the region about the ²⁸Al photopeak, and a conversion gain for 512 channels was used so that analyser dead time was only 1–2%.

The actual elapsed counting period was kept constant, and was accurately timed by means of a crystal-controlled time base. The live time was recorded in the first channel of the analyser memory.

Irradiation and delay times were preset at 60 sec each. The rabbit was loaded into the pneumatic system and the automatic irradiation cycle initiated. After a preset delay time, the deuteron beam was turned on. The integrated relative neutron dose, measured by the boron trifluoride detector was recorded on a six-decade scaler,

gated by the timing circuit controlling the neutron generator. The same circuit regulated the dry nitrogen jet which spun the rabbit.

The actual length of the irradiation period was recorded by a electromechanical clock.

At the end of the irradiation, the rabbit was returned to the counting position. After the preset delay to allow ^{16}N activity to decay, the time base was enabled, starting the 300-sec counting period.

The recorded spectrum and elapsed live time were read out on to punched paper tape, and converted to punched cards for computer processing. Irradiation and delay times, and the integrated boron trifluoride count, were manually recorded and transferred to computer cards.

Calculation of results

Oxygen. A computer program OXYCALC was used for data reduction. Details of weight and type of material in each irradiation capsule, together with an index number indicating whether the rabbit was a sample, standard or blank, were read in first. These were referenced for use in the calculation by the rabbit number.

Each multiscaler record was inspected for the start and end of the BF_3 count. Each channel in this period was treated as an individual neutron irradiation. The growth factor, G , was given by

$$G = (1 - e^{-\lambda \Delta T})$$

where λ is the ^{16}N decay constant and ΔT is the multiscaler dwell time. The decay during each subsequent channel was constant and was described by a decay factor, D , such that

$$D = (e^{-\lambda \Delta T})$$

The ^{16}N activity induced during any time interval represented by a single channel, J , containing a BF_3 count $B(J)$, was proportional to $G \cdot B(J)$. The observed ^{16}N activity was corrected for flux variations in the following way. The term $G \cdot B(1)$ represented the integrated induced activity $I(1)$, at the end of the first dwell time period. At the end of the second dwell time interval, the integrated activity, $I(2)$, was represented by $D \cdot I(1) + G \cdot B(2)$. In the general case

$$I(J) = (D \cdot I(J-1) + G \cdot B(J))$$

The operation of the neutron beam was not synchronized with the multiscaler and irradiation did not last for the whole time period in the first and last channels. The calculation averaged the neutron dose over the whole dwell time for these two channels, but for short dwell times the error introduced was trivial.

At the end of the irradiation record, the beginning of the ^{16}N γ -count was sought. The multiscaler was running during the transfer of the activated rabbit, and one or two of the initial channels usually contained anomalously low counts. The channel containing the highest number of γ -ray counts was therefore taken as the true beginning of the ^{16}N count. The first 40 channels of the γ -count were corrected for decay to the midpoint of the channel representing the start of the ^{16}N decay curve, and a weighted summation made. The expected integrated activity calculated from

the relative neutron dose was similarly corrected, and the weighted sum of the actual ^{16}N γ -counts was normalized to this number. An empirical correction was made for the activity of the empty rabbit.

Silicon. Abundances were derived with the COMSTAR program. Spectra were read in and corrected for the instrumental background. The area of the photopeak was evaluated by the method outlined by STERLINSKI¹⁵, whose eqn. (7) was rewritten in the form

$$S_n = n \cdot a_0 + \sum_{i=1}^n (n - 2i + 0.5) (a_{+i} + a_{-i})$$

where n is the number of channels integrated, channel 0 being the middle channel of the photopeak; a_{+i} , a_{-i} are the counts in the i th channels above and below the middle channel respectively. The computer program selected the center of the peak, and performed the integration for increasing values of n . The variance, V_{sn} , was calculated from:

$$V_{sn} = n^2 a_0 + \sum_{i=1}^n (n - 2i + 0.5)^2 (a_{+i} + a_{-i})$$

and the value of S_n with the minimum relative variance selected for the abundance calculation. The integrated peak area was normalized for BF_3 integrated count and irradiation, decay and live times.

The integration method can compare standard and sample spectral shapes to detect non-linearities in the sample spectrum underneath the photopeak. A linear regression was fitted to the ratio of sample to standard peak areas, with the integration width as the independent variable. The slope of the line was tested for significance by means of null hypothesis model. Significant slopes were not found, indicating a straight base line beneath the photopeak.

Sample and standard comparison

Results for oxygen and silicon were calculated according to three comparison models.

Dual standards. The activity of the sample was normalized to the mean of the activities of the nearest preceding and following standards. This method was preferred when analyses were made under conditions of serious beam instability.

Linear regression. A least-squares fit was made to the normalized activities of the standards in any series of irradiations, with run number as the independent variable. Conditions where the beam was decaying appreciably but smoothly were suitable for treatment by this model. It could be further sophisticated by fitting a polynomial to the data, rather than restricting the fit to a linear regression.

Comparison factor. The mean of the normalized activities of the comparator standards was used for the calculation of the sample abundances. Clearly, if the standard activities are sufficiently reproducible there is considerable statistical advantage to this approach. Provided that the generator and monitoring systems were operating in a stable manner, this method of calculation was superior to the other two models.

RESULTS AND DISCUSSION

The results of analyses of the Allende chondrite for oxygen are given in Table IV. The errors quoted are standard deviations for a single determination calculated from the replicate analyses and are *not* derived from counting statistics. For oxygen, the mean relative deviation for a single determination, derived from counting statistics, is about 2%. Table IV shows that the comparison factor method yields more precise replicates than the dual standard or linear regression methods. The mean relative deviation for a single determination calculated by the comparison factor model is 2.0% and agrees well with that determined from counting statistics. Random errors from other sources are therefore very small. The reproducibility of the replicate analyses for oxygen in each Allende sample approaches that obtained with a refined biaxial rotator system by LUNDGREN AND NARGOLWALLA⁶ for the comparison of pure benzoic acid and oxalic acid standards.

TABLE IV

14-MeV NEUTRON ACTIVATION ANALYSES OF OXYGEN IN THE ALLENDE CHONDRITE

Sample number	Rabbit number	Number of analyses	Dual standard	Linear regression	Comparison factor
S-5211a	1845	6	36.3 \pm 1.3	36.4 \pm 1.3	36.2 \pm 0.7
	1846	6	35.3 \pm 1.6	34.9 \pm 1.4	34.9 \pm 1.0
	1847	6	35.7 \pm 1.1	35.7 \pm 0.7	35.6 \pm 0.4
S-5211b	1848	6	36.4 \pm 1.5	36.2 \pm 1.1	36.2 \pm 1.2
S-5207a	1849	6	35.6 \pm 0.8	35.7 \pm 0.9	35.7 \pm 1.0
S-5207b	1850	6	36.8 \pm 0.8	36.9 \pm 0.5	36.9 \pm 0.5

TABLE V

14-MeV NEUTRON ACTIVATION ANALYSES OF SILICON IN THE ALLENDE CHONDRITE

Specimen number	Rabbit number	Number of analyses	Dual standard	Linear regression	Comparison factor
S-5211a	1845	6	16.05 \pm 0.22	15.98 \pm 0.15	15.98 \pm 0.14
	1846	6	15.49 \pm 0.17	15.47 \pm 0.13	15.48 \pm 0.13
	1847	6	15.64 \pm 0.14	15.66 \pm 0.14	15.66 \pm 0.14
S-5211b	1848	7	16.36 \pm 0.35	16.38 \pm 0.26	16.39 \pm 0.24
S-5207a	1849	7	15.93 \pm 0.27	15.87 \pm 0.20	15.89 \pm 0.11
S-5207b	1850	7	16.28 \pm 0.24	16.26 \pm 0.14	16.26 \pm 0.11

The results for silicon in the Allende chondrite are listed in Table V. Errors are standard deviations for single determination calculated from the replicate determinations on each sample. Again the best precision was obtained by the comparison factor method, where the mean relative deviation for all the samples was 0.9%. The relative standard deviation expected from counting statistics is 0.4-0.5%, indicating a small contribution from random errors elsewhere in the analytical system. Some of the variation is probably due to the higher background in the 1.78-MeV region, and to small interferences from other 14-MeV neutron irradiation products.

The preceding discussion has been confined to the variation of replicate analyses for the same sample. These will now be compared with the errors between

TABLE VI

MEAN OXYGEN AND SILICON ABUNDANCES IN THE ALLENDE CHONDRITE

Sample number	Number of samples	Abundance (%)				Comparison factor	
		Dual standard		Linear regression			
		Oxygen	Silicon	Oxygen	Silicon	Oxygen	Silicon
S-5211a	3	35.8 \pm 0.5	15.73 \pm 0.29	35.7 \pm 0.8	15.70 \pm 0.26	35.6 \pm 0.7	15.70 \pm 0.25
S-5211	4	35.9 \pm 0.5	15.89 \pm 0.40	35.8 \pm 0.7	15.87 \pm 0.40	35.7 \pm 0.6	15.88 \pm 0.40
S-5207	2	36.2 \pm 1.2	16.11 \pm 0.35	36.3 \pm 1.2	16.07 \pm 0.39	36.3 \pm 1.2	16.08 \pm 0.37
Mean		36.0 \pm 0.6	15.96 \pm 0.35	36.0 \pm 0.7	15.94 \pm 0.35	35.9 \pm 0.7	15.94 \pm 0.35
Fluorine correction		0.001	—	0.001	—	0.001	—
Phosphorus correction		—	0.05	—	0.05	—	0.05
Iron correction		—	0.08	—	0.08	—	0.08
Corrected S-5211		35.9	15.76	35.8	15.74	35.7	15.75
Corrected S-5207		36.2	15.98	36.3	15.94	36.3	15.95
Corrected mean		36.0	15.83	36.0	15.81	35.9	15.81

different samples, which are summarized for both elements in Table VI. Standard deviations are calculated from the mean values for each sample. In the case of S-5207 where only two samples were analysed, the quoted error is simply the difference between the two values.

The variation between samples is considerably larger than would be expected for a homogeneously ground, well-mixed powder. A large variation between different pieces is reasonable, as the Allende chondrite does contain sporadically distributed

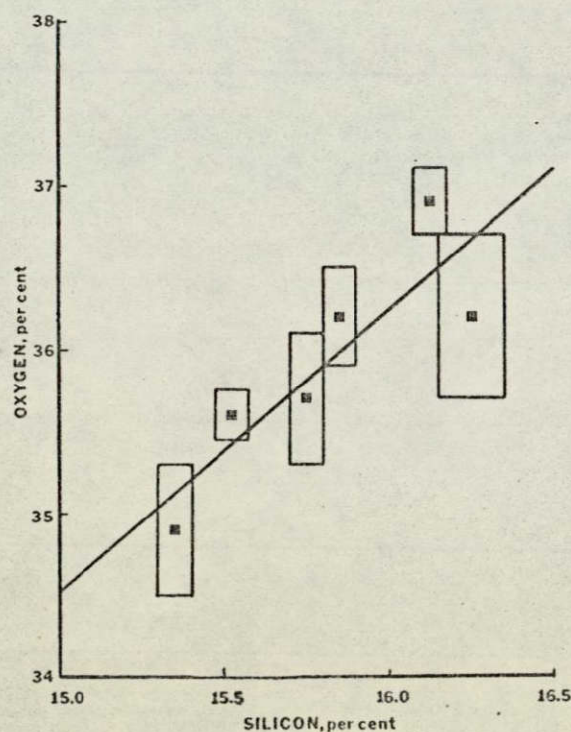


Fig. 1. Correlation of oxygen and silicon abundances in six samples of the Allende chondrite.

TABLE VII

OXYGEN AND SILICON IN TWO USGS STANDARD ROCKS

Standard rock	Rabbit number	Number of analyses	Dual standard		Linear regression		Comparison factor	
			Oxygen	Silicon	Oxygen	Silicon	Oxygen	Silicon
AGV-1	1821	6	47.9 ± 1.2	27.77 ± 0.62	48.1 ± 1.0	27.71 ± 0.66	48.3 ± 0.9	27.79 ± 0.75
	1822	6	47.7 ± 1.0	28.19 ± 0.45	47.8 ± 0.6	28.04 ± 0.46	47.8 ± 0.5	28.19 ± 0.54
	1823	6	47.4 ± 1.3	27.76 ± 0.37	47.6 ± 0.8	27.75 ± 0.42	47.6 ± 1.2	27.78 ± 0.56
Mean			47.7 ± 0.24	27.91 ± 0.25	47.8 ± 0.27	27.83 ± 0.18	47.9 ± 0.36	27.92 ± 0.23
Fluorine correction			0.02	—	0.02	—	0.02	—
Phosphorus correction			—	0.10	—	0.10	—	0.10
Iron correction			—	0.02	—	0.02	—	0.02
Corrected mean			47.7	27.79	47.8	27.71	47.9	27.80
BCR-1	1824	6	45.7 ± 0.9	26.11 ± 0.50	45.8 ± 0.8	26.11 ± 0.44	45.8 ± 0.9	26.17 ± 0.67
	1825	6	45.8 ± 0.5	25.48 ± 0.28	45.7 ± 0.4	25.51 ± 0.22	45.6 ± 0.4	25.53 ± 0.36
	1826	6	46.0 ± 0.7	25.69 ± 0.56	46.0 ± 0.7	25.75 ± 0.45	45.9 ± 0.5	25.74 ± 0.66
Mean			45.8 ± 0.15	25.75 ± 0.33	45.8 ± 0.16	25.79 ± 0.30	45.8 ± 0.14	25.81 ± 0.31
Fluorine correction			0.02	—	0.02	—	0.02	—
Phosphorus correction			—	0.07	—	0.07	—	0.07
Iron correction			—	0.03	—	0.03	—	0.03
Corrected mean			45.8	25.63	45.8	25.69	45.8	25.71

inclusions of widely varying compositions². Three of the samples, however, were aliquots of the same powder (S-5211a), but their standard deviation is very close to that for six samples of four different pieces. Apparently, homogeneous mixing of a sample containing silicates of differing composition, sulphides and some free metal is not a trivial problem.

Silicon and oxygen are largely in the same phases in chondrites. Table VI indicates that their abundances are correlated. This is clearly seen in Fig. 1, where the mean abundance for each sample is plotted. Error boxes represent the standard deviations of the means and the regression line was calculated from the unweighted means with silicon as the independent variable. The correlation coefficient, $r=0.86$, indicates a highly significant correlation between these two elements.

The large variation between samples and the correlation between silicon and oxygen observed in the case of the Allende chondrite is in contrast to the results for well mixed rock powders. Results for the USGS standard andesite, AGV-1 (split 110, position 21) and standard basalt, BCR-1 (split 1, position 8) are shown in Table VII. These analyses indicate the high precision which can be obtained with well mixed powders. For both elements the deviation of the mean of three aliquots is significantly lower than the deviations of the individual replicates for each powder. The silicon analyses were made under conditions of severe beam instability, and illustrate the reproducibility of the mean of six analyses even under less than ideal circumstances. These silicon results again show how the dual standard model gives better precision for individual replicate runs when the beam is unstable. Although the analyses for the two standard rocks should not be taken as definitive, it is interesting to compare oxygen and silicon abundances reported here with those of other workers. These are summarized in Table VIII.

The silicon abundances reported here for Allende agree reasonably well with the chemical analysis made at the Smithsonian Institution by CLARKE *et al.*¹². The specimens S-5207 were obtained from this Institution, and the mean value found for these (Table VI) agrees very well with the chemical results. Agreement is less satisfactory with the silicon abundances reported by KING *et al.*¹¹. The spectrophotometric value falls within the range of abundances found in the present work, but the spectrographic results are significantly lower.

The agreement between the direct oxygen analysis in Allende and that determined from the full major element analysis is reasonable. The presence of sulphides, free metal and unusual mineral phases introduces some uncertainty when major elements are reported as oxides and may partly account for the difference observed. The agreement is better with the S-5207 results than with the mean of all samples.

Agreement between silicon analyses of andesite AGV-1 and basalt BCR-1 is acceptable particularly when the wide range of values making up FLANAGAN'S¹⁶ average is considered. The oxygen values reported here are higher than values calculated from total major element analyses by 0.3–0.6% oxygen. Strangely enough, the other 1.4-MeV neutron activation results⁴ are lower than the chemical values by 0.4–1.0 absolute % oxygen. VOLBORTH AND VINCENT⁴ discussed the problems of accurate direct oxygen determination and stressed the role of "minus" water (H_2O-), *i.e.* the water released by heating to 110°. Analyses for H_2O- summarized by FLANAGAN¹⁶ range from 0.8 to 1.3% in AGV-1 and from 0.3 to 1.0% in BCR-1. These differences are of the same order as the discrepancies in the oxygen analyses. It is clear that in a

TABLE VIII

COMPARISON OF OXYGEN AND SILICON RESULTS FOR THE ALLENDE CHONDRITE AND TWO USGS STANDARD ROCKS

Method	Abundance (%)					
	Allende		AGV-1		BCR-1	
	Oxygen	Silicon	Oxygen	Silicon	Oxygen	Silicon
Compilation ^a	—	—	47.3	27.58	45.5	25.47
Spectrographic ^b	—	14.49	—	—	—	—
Spectrophotometric ^b	—	15.59	—	—	—	—
Chemical ^c	36.9	16.00	—	—	—	—
14-MeV neutron activation ^d	—	—	46.9	27.85	44.5	25.43
14-MeV neutron activation ^e	36.0	15.83	47.7	27.79	45.8	25.63
14-MeV neutron activation ^f	36.0	15.81	47.8	27.71	45.8	25.69
14-MeV neutron activation ^g	35.9	15.81	47.9	27.80	45.8	25.71

^a FLANAGAN¹⁶; oxygen calculated from total analysis.^b KING *et al.*¹¹.^c CLARKE *et al.*¹².^d VOLBORTH AND VINCENT⁴ for oxygen; VINCENT AND VOLBORTH⁵ for silicon.^e This work, dual standard model.^f This work, linear regression model.^g This work, comparison factor model.

definitive study of oxygen in standard rocks, determination of H₂O— and drying of samples at 110° before irradiation is essential.

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SUMMARY

Improved methods for the determination of oxygen and silicon by 14-MeV neutron activation are described. A single-transfer system is employed to attain a precision approaching that of biaxial rotator systems. Analyses of six samples of the Allende chondrite are given and a correlation is found between oxygen and silicon abundances.

RÉSUMÉ

On décrit des méthodes pour le dosage de l'oxygène et du silicium par activation neutronique 14-MeV. Un système "transfer simple" est utilisé pour arriver à une précision voisine de celle des systèmes "rotateur biaxial". Les résultats d'analyse de 6 échantillons sont donnés.

ZUSAMMENFASSUNG

Es werden verbesserte Methoden zur Bestimmung von Sauerstoff und Silicium mit Hilfe der 1.4-MeV-Neutronenaktivierung beschrieben. Um eine Genauigkeit zu erreichen, die derjenigen des Biaxial-Rotator-Systems entspricht, wurde ein Single-Transfer-System verwendet. Die Analysen von 6 Proben von chondritischen Meteoriten werden angegeben. Eine Zusammenhang zwischen den Sauerstoff- und Siliciumüberschüssen wird gefunden.

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Anal. Chim. Acta, 49 (1970) 287-299

SECTION IX

List of Additional Publications Supported in Part by this Contract and Papers Currently in Press

(Note: Reprints or copies of these manuscripts may be obtained on request.)

1. W. D. Ehmann and J. W. Morgan, Precise Non-Destructive Determination of Some Major Elements in Lunar Material by 14 MeV Neutron Activation, Proceedings of the Second Oak Ridge Conference on the Use of Small Accelerators for Teaching and Research, Oak Ridge Associated Universities, Oak Ridge, Tennessee, March 23-25, 1970, CONF-700322, pp. 205-220 (1970).
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3. W. D. Ehmann, D. M. McKown, and J. W. Morgan, Coincidence Counting Applied to the Activation Analysis of Meteorites and Rocks, Proceedings of the N.A.T.O. Advanced Study Institute - Activation Analysis in Geochemistry and Cosmochemistry, Kjeller, Norway, September 7-12, 1970, Universitetsforlaget, Oslo, In Press.
4. J. W. Morgan and W. D. Ehmann, 14 MeV Neutron Activation Analysis of Rocks and Meteorites, Proceedings of the N.A.T.O. Advanced Study Institute - Activation Analysis in Geochemistry and Cosmochemistry, Kjeller, Norway, September 7-12, 1970, Universitetsforlaget, Oslo, In Press.

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